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THERMAL THEORY OF COMBUSTION AND EXPLOSION

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THERMAL THEORY OF COMBUSTION AND EXPLOSION*

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INTRODUCTION

In his "Outlines of Dynamic Chemistry" of 1884, van't Hoff formulated the basic laws governing the progress of simple chemical reactions. For the case of mutual interaction of two sets of particles, the velocity of reaction is proportional to the number of collisions between the molecules - that is, to the square of the number of molecules per unit volume, if the reaction is between the same kind of molecules ($2\text{Cl}_2\text{O} = 2\text{Cl}_2 + \text{O}_2$), and to the product of the numbers of molecules if the reaction is between molecules of different kinds ($\text{H}_2 + \text{I}_2 = 2\text{HI}$). Van't Hoff denoted reactions of this type as bimolecular (or reactions of the second order).

In the case where the molecule breaks up in the interval of free flight between impacts ($\text{CH}_3\text{NNCH}_3 = \text{C}_2\text{H}_6 + \text{N}_2$), the reaction velocity will be proportional to the first power of the number of molecules per unit volume. Reactions of this type, van't Hoff denoted as monomolecular (or reactions of the first order).

The constant of the reaction velocity increases with the temperature, according to the exponential law $e^{-\frac{E}{RT}}$ where T is the absolute temperature, R the gas constant, equal to 2 cal/deg, and E a magnitude which is characteristic of each reaction (determining the rate of increase of the velocity with the temperature). Arrhenius, some years later, demonstrated in greater detail the correctness of this temperature law and gave a simple explanation, based on the kinetic theory, of the magnitude E , which he called the energy of activation. He assumed that not all molecules took part in the reaction - only those in an active state - the energy imparted to a molecule in the active state being greater than a certain amount E . According to the Boltzman law, the number of active mole-

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cules constitute a fraction $e^{-\frac{E}{RT}}$ of the inactive molecules. It follows that the velocity of reaction expressed in terms of the number of reacting molecules per unit time per unit volume will be

$$w = \frac{dx}{dt} = (a - x)^n e^{-\frac{E}{RT}}$$

where $n = 2$ for bimolecular and $n = 1$ for monomolecular reactions. (x is the number of activated molecules at a given instant t .) At the start of the reaction when

$x = 0$, $w_0 = ka^n e^{-\frac{E}{RT}}$. (a is the number of molecules of the initial substance per unit volume at the start of reaction.) The constant k for bimolecular reactions is, evidently, equal to $\sqrt{2\pi} \sigma^2 u$ where σ is the diameter and u the thermal velocity of the molecule. In the case of monomolecular reactions $k \approx \nu$ where ν is the number of vibrations of the molecule for the type of molecular bond that is broken - that is, a magnitude of the order of $10^{13} - 10^{14}$.

Five years ago Eyring, on the basis of modern statistical methods and data on the structure and energy of the molecule, considered this problem (theory of an activated complex) and for simple cases arrived at practically the same result as that given above. For more complex molecules entering bimolecular reactions, he showed the possibility of a small steric factor appreciably decreasing the magnitude k and gave a method for the approximate evaluation of this factor. For monomolecular reactions, Eyring showed that in certain (very special) cases the constant k may exceed the value 10^{14} , the value, however, remaining $10^{13} - 10^{14}$ for most actual processes. Thus, for elementary reactions, the theories of van't Hoff and Arrhenius have retained their full validity up to the present. In the light of recent developments, however (in particular, the theory of chain reactions), the actual processes involved are more complicated than appeared to the founders of the early theory. The elementary stages of a complex reaction (with various intermediate products) follow the laws of van't Hoff and Arrhenius, but the reaction as a whole often follows laws very different from the simple relations for bimolecular and monomolecular processes. A law of wide application, for example, for the initial phases (20 to 30 percent) of the transformation in a large

number of exothermic reactions, is $w = Ae^{\varphi t}$ where φ depends on the concentration of the initial substances and increases as $e^{-\frac{E}{RT}}$ with the temperature. In this case the velocity of reaction as a function of the concentration of initial substances is $\frac{dx}{dt} = w = kx$; that is, the velocity of reaction in its first phases is proportional to the quantity of the substances reacting at the given instant of time. In many cases this law may be generalized for the entire transformation process in the form

$$w = k(a - x)x e^{-\frac{E}{RT}}$$

Such laws are typical for the majority of thermal reactions in oxygen and air. In many cases the velocity of a complicated reaction depends on the square root of the concentration of one of the different kinds of molecule taking part in the reaction. Thus, for the reaction of hydrogen with bromine

$$w = k(H_2) \sqrt{(Br_2)} e^{-\frac{E}{RT}}$$

where the symbol in parentheses indicates the number per unit volume of the molecules indicated.

Cases are encountered, however, where the complex reaction formally leads to the same type of laws as for simple monomolecular and bimolecular reactions, although the meaning and magnitude of the constant k is now different and the energy of activation E is made up of the sum of the energies of the elementary processes constituting the complex reaction. Thus, the disintegration of many organic substances is formally represented by the law

$w = kae^{-\frac{E}{RT}}$, but there is no doubt that this reaction follows a series of monomolecular, bimolecular, and trimolecular stages. Fortunately, for all our considerations below, we require only the formal, experimentally obtained expression for the reaction velocity as a function of the initial concentration and temperature, and there is no need for knowing the actual mechanism of the process.

The mathematical treatment of the results is most simple for those cases where we deal with formal laws of reactions of the first and second order; hence we shall consider these mainly.

After the above brief remarks on the chemical kinetic theory, we now pass to the subject proper of our paper, namely, the present state of the thermal theory of combustion and explosion. It may be remarked incidentally that these phenomena are so widespread, so intensively utilized in engineering practice (heating, internal-combustion engines, explosives) that the theoretical principles underlying combustion and explosion should be made part of a general course of physical-science instruction together with courses on heat conduction and thermodynamic cycles. The reason for the absence of these subjects in the general course may be ascribed to the lack of scientific analysis of these phenomena. Within the last ten years, however, mainly as a result of the work of Soviet scientists on the fundamental principles of the theory of combustion and explosion, a start has been made toward filling the gap. As we shall see below, the theory of these phenomena is not fundamentally complicated and is in a form that may be successfully presented to students. Unfortunately, in the existing literature on the subject, there is only one attempt at a systematic presentation of the theory of the above-mentioned phenomena on the basis of our work and the work in foreign countries. That is the recently published book by Jost (reference 2). No such book exists in the Russian language. For this fact the author and his coworkers are to blame inasmuch as we are responsible to a considerable extent for the theory. The present paper is an attempt - at least, partially - to make good the defect by outlining briefly the theory of combustion and explosion. Of course, the question as to the necessity for a detailed monograph on this branch of science still remains.

The question as to the nature of the self-ignition phenomenon that occurs in a combustible gas with rise in temperature up to the "self-ignition temperature" was first considered by van't Hoff in 1883 in his before-mentioned book "Outlines of Chemical Dynamics." In that book van't Hoff gives a generally correct qualitative formulation of the causes of the phenomenon. We shall here quote from the corresponding section of his book:

"One of the conclusions of the preceding chapter deserves special attention since it is in apparent contradiction with the phenomenon of ignition. The experiments just referred to on the effect of the temperatures on the velocity of reaction lead to the assumption of the continuity of this phenomenon, a continuity derived both as a

result of the experiments described and the theoretical considerations to which I referred. The phenomenon of ignition, however, occurring suddenly at a given temperature, apparently shows that the assumed continuity of the process admits of an exception. Meyer, for example, in regard to this question, expresses himself as follows:

"The start of the reaction may, in general, be considered to be the instant of lowest temperature at which a definite chemical transformation still takes place and which is generally denoted as the ignition point when dealing with combustible substances."

We find here an obvious contradiction to the considerations on the effect of the temperature on the velocity of reaction. Actually these considerations exclude any sudden acceleration and require that the chemical change, if occurring at a given temperature, should occur also at other temperatures, though at a different velocity. Closer examination of the problem shows that the ignition phenomenon in no way requires the existence of a definite temperature at which the reaction begins. In this case the phenomenon fits in completely with the theory developed above.

This reasoning is based on three conditions which should be satisfied for every chemical transformation capable of leading to ignition. Before presenting these conditions, I may remark that under the term 'ignition' I understand not only the explosive phenomenon but the entire transformation which occurs with a local rise in temperature up to the so-called 'ignition temperature.' In every phenomenon of this kind we see that the following conditions are satisfied:

1. The transformation is accompanied by heat liberation.
2. The transformation occurs at a more or less slower rate at temperatures lower than the ignition temperature.
3. The transformation is accelerated with increase in the temperature.

"With these three conditions satisfied a phenomenon such as ignition can occur. In order to show this, let us suppose that at a certain point of the medium not subject

to chemical change - for example, the atmospheric air - the temperature is raised from 0 to T . When the heat source is removed the temperature rise will be gradually spread as a kind of heat wave. This wave will be propagated with a definite velocity, the temperature dropping more and more to zero. The graphical presentation of the relation between the temperature and the distance from the starting point 0 is given by the curve T_1A_1 (fig. 1) - temperatures being given along OT and distances along OD. For brevity we shall denote by ΔT the decrease in temperature in the heat wave a short time after the start.

"We shall now suppose that in the medium considered, a chemical change is possible and that it satisfies the three conditions above - substituting, for example, a combustible mixture for the atmospheric air. The local increase in temperature will then give rise to the above-described wave, with this difference only, that the temperature will decrease at a slower rate on being propagated, especially at the start, because the chemical change brought about by the rise in temperature results in heat liberation. The value of ΔT is thus decreased and the graphical representation of the heat wave for this case is that given by curve T_1A_1 (fig. 2).

"We shall now determine the effect of a rise in temperature in both cases. As regards the medium, not subject to chemical action (atmospheric air), what occurs simply is that in the heat wave the lowering of the temperature ΔT will be greater (as indicated by the curve T_2A_2 (fig. 1)) due to the greater differences in temperature between the wave and the medium in which it is propagated. The assumption of the possibility of chemical change (combustible mixture) leads simultaneously to this effect, by which ΔT is increased, and to the other effect, by which ΔT is decreased. In fact, the chemical reaction, accelerated by the higher temperature of the wave, will in this case give a greater heat liberation. Thus, if the slowing action prevails, the value of ΔT will decrease with rise in the temperature.

"With the above facts in mind, we can predict that there is a certain temperature T_3 (fig. 2) for which the value of ΔT becomes zero or, in other words, the temperature at which the heat wave is propagated is constant as indicated by the horizontal line T_3A_3 in figure 2. In exactly the same manner a still higher initial tempera-

ture T_3 gives rise to a heat wave whose temperature, instead of decreasing, increases to a value at which the complete chemical action can occur. Such a process is indicated by the curve T_3A_3 (fig. 2).

"It is evident that waves with decreasing temperature give rise to only a very small chemical action while waves with increasing temperature lead to complete chemical action. Consequently, the temperature T_3 which gives a constant temperature wave corresponds to the ignition temperature.

"It would not be difficult to express all that has been said above by a mathematical formula but I prefer to express the result as follows: The ignition temperature is that temperature at which the initial loss in heat due to heat conduction, and so forth, is equal to the heat liberated at the same time by the chemical transformation.

"From the above considerations it appears to me that the ignition phenomenon is completely accounted for by the effect of the temperature on the velocity of reaction." (See van't Hoff's "Outlines of Chemical Dynamics," pp. 111-113.)

Although van't Hoff here gave no quantitative formulation of the ignition phenomenon and even his qualitative treatment is far from accurate, nevertheless he did correctly establish the physical nature of the phenomenon. He was the first to show that ignition is the result of a reaction which - if a certain amount of heat is liberated (that is, if the mixture is heated to the corresponding temperature) in order that the heat may not be conducted away by the walls - leads to an abrupt rise in temperature and velocity of reaction, a process which we denote as explosive. There is thus no contradiction between the phenomenon of self-ignition and the continuity of the change in velocity of reaction with temperature rise. The phenomenon of self-ignition is the result of the dependence of the speed of reaction on the temperature if account is taken of the heating which arises in exothermic reactions and which leads to a change of temperature with time.

It is a curious fact that for forty years the view held by van't Hoff on the nature of self-ignition was not mathematically formulated in any clear manner - this in spite of the fact that the concept of ignition tempera-

ture was very often made use of as a certain constant of the substance (for example, in the theory of flame propagation), although from the analysis of van't Hoff and from experimental determination of this magnitude, it was evident that the ignition temperature is not a constant but depends on the conditions under which the heat is liberated.

In 1927-28 the author succeeded, by very simple means, in giving a mathematical formulation to the theory of van't Hoff (reference 3). The author at that time was unfamiliar with the work of van't Hoff and arrived at his conclusions by the method of analogy - applying his results and those of A. F. Walter in the field of dielectric breakdown to the ignition problem. It is very instructive to note how the same physical factors and considerations may be applied to quite different natural phenomena. For this reason I should like to dwell briefly on our work on the thermal puncture of dielectrics. The conductivity of a dielectric increases with the temperature according to the same law that governs the speed of chemical reactions. When a voltage is applied to a dielectric, then according to Joule's law, heat is developed which is proportional to the conductivity times the square of the applied potential difference. On increasing the potential difference the amount of heat developed may become so large, however, that the thermal equilibrium is upset. The dielectric then begins to heat up gradually, as a result of which the electrical conductivity increases and still more heat is developed until finally the flow of heat is so great that the dielectric melts and evaporates, that is, it punctures. The above considerations are the physical basis of the thermal theory of dielectric breakdown - very similar, as we see, to the thermal theory of explosion.

An essential difference, however, is constituted by the fact that the dielectric does not all melt but the puncture occurs along a narrow, cylindrical channel in the form of a filament between the two electrodes. This led Wagner, who in 1910 first presented the thermal theory of dielectric breakdown, to formulate the theory incorrectly. (He considered the heat liberated, not in the electrodes, but in the dielectric along the surface of the channel through which the puncture occurs.) Walter, Fock, the author in Russia, and Rogovsky in Germany, independently of one another, first formulated the correct thermal theory of dielectric breakdown.

The explanation for the filament-shaped puncture was as follows: We assumed that the dielectric was all heated by the current and that the heat was given off chiefly at the electrodes. As a result, however, of the small temperature gradient in the planes parallel to the electrodes the breakdown of the thermal equilibrium first occurs at the center where the temperature is greater - though by a small amount - than that at the edges. As soon as the abrupt increase in the temperature in the central part of the dielectric starts, the electric conductivity increases so rapidly that the potential difference on the electrodes drops automatically, as a result of which the remaining parts of the dielectric are not punctured. Only in this circumstance is there a difference between dielectric puncture and thermal explosion. This difference does not, however, concern the conditions under which breakdown in the thermal equilibrium occurs but relates to the manner in which the phenomenon develops after the breakdown of equilibrium has already occurred. A number of considerations led to the conclusion that in the case where the initial electrical conductivity is large and puncture occurs at a low voltage, the conditions for the formation of a filament-shaped puncture become less favorable and we may then directly observe the breakdown in equilibrium throughout the dielectric leading to melting and vaporization of a considerable portion of it. At sufficiently high temperatures in the dielectric breakdown of rock salt a considerable portion of the substance is actually vaporized and the punctured hole is about the width of a finger. For gelatine this phenomenon may be observed at room temperature.

From the mathematical formulation of the theory a number of results were arrived at. (The temperature coefficient of the puncturing voltage should be equal to half the temperature coefficient of the electric conductivity; the puncturing voltage should drop according to a definite law as a function of the change in thermal conductivity, electrodes, etc.) All these results were strictly confirmed by the tests of Walter and Inge, by whom the thermal theory of dielectric breakdown was finally established.

When the author in 1927 interested himself in the phenomenon of explosion, he immediately discerned the analogy of this phenomenon with that of thermal puncturing of dielectrics. If, during the breakdown, the amount of heat generated by the current per unit volume is equal to

$q = 0.24 \sigma_0 e^{-\frac{E}{RT}} V^2$, where $\sigma_0 e^{-\frac{E}{RT}}$ is the electric conductivity, V the applied voltage, then for a chemical

$$-\frac{E}{RT}$$

reaction the same magnitude is equal to $q = Q'w = Q'k_{ae}$ where Q' is the heat considered for 1 molecule of the product, a the number of molecules of the initial substance per unit volume (i.e., a magnitude proportional to the gas pressure). Thus in the case of dielectric puncture, if we can find a relation between the puncturing voltage and the temperature we should, in the case of self-ignition, obtain a relation between the self-ignition temperature and the gas pressure.

Below we shall present the heat theory of combustion and explosion, dividing the work into three parts: 1) the thermal theory of self-ignition, 2) the theory of ignition by hot bodies, and 3) the theory of flame propagation; and shall illustrate the theoretical with the experimental results - few of which, however, are available. The entire theory was developed over a number of years at the Institute of Physical Chemistry by Semenov, Todes, Zeldovich, Frank-Kamenetsky, and partly by Belaev, Appin, and Chelkin. The experimental illustrations are taken from the investigations of our institute (Zagulin, Neiman, Roginsky, Belayev, Appin, and others), and from the work in other countries.

The present paper is concerned only with thermal ignition and combustion, and no treatment is given of the general and very interesting subject of chain self-ignition and the propagation of flames, to which subject a separate article will be devoted.

I. THERMAL SELF-IGNITION*

In a reaction in the gaseous phase with velocity w , measured by the number of molecules of the product appearing per second per unit volume, the amount of heat given off per second in the entire volume v of the vessel is

$$q_1 = v Q' w$$

where Q' is the heat liberated by each elementary process of the reaction; that is, $Q' = Q/N$, where Q is the heat of the reaction for one gram-mol of the product, and

*The entire theoretical part is based on the work of Semenov, Todes, and Frank-Kamenetsky (references 3, 4, and 5).

N the Avogadro number ($N = 6 \times 10^{23}$). As has been shown, the velocity of the reaction at the initial stage as a function of the absolute temperature T and the number of molecules a of the initial substance per unit volume is equal to $w = k_1 a e^{-\frac{E}{RT}}$ for monomolecular, and $k_2 a^2 e^{-\frac{E}{RT}}$ for bimolecular reactions, so that

$$q_1 = \frac{v Q k a^n e^{-\frac{E}{RT}}}{N} \quad (1)$$

where for monomolecular reactions $n = 1$, and for bimolecular reactions $n = 2$.

The amount of heat conducted away by the walls of the vessel will be

$$q_2 = \chi (T - T_0) S \quad (2)$$

where χ is the coefficient of heat conductivity, T the temperature of the reacting gas, T_0 the vessel-wall temperature applied from the outside, and S the area of the walls.

Figures 3 and 4 show q_1 and q_2 as functions of the temperature. Figure 3 corresponds to the case where the vessel wall is subject to a temperature T_0 and the pressure of the reacting gas changes - that is, the magnitude a in formula (1). Curve 1 corresponds to the smallest value of a , namely, a_1 ; curve 2, to a medium value a_2 ; and curve 3, to the largest value a_3 . For $a = a_1$ the gain in heat q_1 is at first larger than the heat loss q_2 . As a result, the gas will be heated to a higher temperature than that of the walls of the vessel. This situation continues, however, only up to the instant that the temperature of the gas reaches a certain value T'_1 (intersection of the curves q_1 and q_2) where $q_1 = q_2$. Beyond this point the gas will not further heat up because for $T > T'_1$ the heat conducted away, q_2 , will be greater than the heat gain, q_1 , and if, for some reason, the gas temperature were to become greater than T'_1 , it would again cool down to the same temperature T'_1 .* Thus for the case consid-

*Only in the case where we artificially heat the gas (for example, by adiabatic compression) to a temperature higher (Continued on p. 12.)

ered, the reaction does not lead to self-ignition and the action is limited to the heating of the gas up to the temperature T'_1 - somewhat higher than that of the walls of the vessel.

For the same temperature T_0 , if the pressure in the vessel were increased to a sufficiently high degree or, what amounts to the same thing, for a sufficiently high value $a = a_3$, q_1 as a function of the temperature will be given by curve 3, which at no point intersects the straight line q_2 . In this case the heat gain q_1 is at all temperatures greater than the heat conducted away q_2 , and thus the gas will be continually heated, the reaction velocity will increase more and more, and we shall then have explosive reaction. Hence for $a = a_3$, thermal self-ignition will take place.

Curve 2 for $a = a_2$ touches the straight line q_2 at one point, and thus separates the region of stationary reaction from the region of self-ignition. The magnitude a_2 or the pressure corresponding to it, p_2 , defines the critical pressure of self-ignition for a given vessel temperature T_0 .

If, keeping the pressure of the gas constant, the wall temperature is varied $T_0^{(1)} < T_0 < T_0^{(3)}$, the behavior of the gas will be represented by figure 4. We now have a single curve of heat gain q_1 and three straight heat-loss lines corresponding to three wall temperatures. By the same considerations as above we may show that for $T_0^{(1)} < T_0$ no self-ignition occurs; for $T_0^{(3)} > T_0$ self-ignition does occur. We denote the temperature T_0 at which the curve q_1 is tangent at one point to the straight line q_2 as the lowest temperature of self-ignition or, simply, the self-ignition temperature for the given pressure p . The point

(Continuation of footnote from p. 11)

than the second point of intersection T'_2 does q_1 again become greater than q_2 and explosive reaction is again possible. This second point of intersection does not give a stable value of the temperature, for if T is slightly less than T'_2 , the temperature drops to T'_1 , and if T is slightly greater than T'_2 , explosion occurs. Thus this second point of intersection is of no significance in the theory of self-ignition and is of interest only in questions of artificial ignition associated with heating of the gas.

of tangency of q_2 and q_1 corresponds to the temperature T_1 ; the difference $\Delta T = T_1 - T_0$ we shall denote as the preignition heating. Between the temperature of self-ignition and the pressure (or the number a) of the mixture, an analytical relation may be derived by making use of the fact that at the point of tangency (for $T = T_1$) $q_1 = q_2$ and also their temperature derivatives $dq_1/dT = dq_2/dT$; that is,

$$\frac{v Q k a^n e^{-\frac{E}{RT_1}}}{N} = \chi (T_1 - T_0) S \quad (3)$$

$$\frac{v Q k a^n e^{-\frac{E}{RT_1}}}{NRT_1} = \chi S$$

From these two equations we can, first of all, find the temperature T_1 at the point of contact as a function of the vessel-wall temperature T_0 . Eliminating χS from both equations, there are obtained:

$$1 = \frac{E}{RT_1^2} (T_1 - T_0) \quad \text{or} \quad \frac{RT_1^2}{E} - T_1 + T_0 = 0$$

$$T_1 = \frac{1 \pm \sqrt{1 - \frac{4RT_0}{E}}}{2 \frac{R}{E}}$$

It is to be noted that for the majority of reactions of interest to us, RT_0/E is a small magnitude not generally exceeding the value 0.05. The self-ignition temperature is generally below 1000°K , and the activation energy E is usually greater than 20,000 calories where, for a low value of E , we have a low ignition temperature and, conversely, for a high value of E , a high ignition temperature. The solution with the positive sign of the radical should be disregarded because then T_1 becomes equal to E/R - that is, has a value of the order of 10000° and above,* and because the solution with the negative sign corresponding to the point of tangency on figures 3 and 4

*The two signs occur because the function $e^{-E/RT}$ has a point of inflection for very high temperatures and for $T \rightarrow \infty$ approaches unity. Hence the straight q_2 lines, on being extrapolated to some tens of thousands of degrees, intersect the curve q_1 a second time (not shown on fig. 3).

gives a much lower temperature T_1 . Thus,

$$T_1 = \frac{1 - \sqrt{1 - \frac{4RT_0}{E}}}{2 \frac{R}{E}} = \frac{2 \left(\frac{RT_0}{E} \right) + 2 \left(\frac{RT_0}{E} \right)^2 + 4 \left(\frac{RT_0}{E} \right)^3 + \dots}{2 \frac{R}{E}}$$

For $\frac{RT_0}{E} < 0.05$, we may disregard the terms of the series starting with $4 \left(\frac{RT_0}{E} \right)^3$, thereby introducing an error of the order

$$2 \left(\frac{RT_0}{E} \right)^2 100\% < 0.0025 \times 2 \times 100\% = 0.5\%$$

of the measured value T_1 .

Thus,

$$T_1 = T_0 + \frac{RT_0^2}{E} \quad (4)$$

and

$$\Delta T_1 = T_1 - T_0 = \frac{RT_0^2}{E} \quad (5)$$

The value ΔT_1 for the case when it is known that ignition does not occur (the temperature T_0 is below the self-ignition temperature), will always be less than $\Delta T_1 = \frac{RT_0^2}{E}$.

Thus if the increment ΔT is less than $\frac{RT_0^2}{E}$, explosion is impossible and, conversely, if $\Delta T > RT_0^2/E$, explosion should take place. For different values of T_0 and activation energy E , the value of ΔT_1 will be different but those cases of interest to us will never, as a rule, exceed a few tens of degrees. Thus, for example, for $T_0 = 700^\circ \text{K}$ and $E = 30,000$ calories $\Delta T_1 = 33^\circ$; for $T_0 = 700^\circ \text{K}$ and $E = 60,000$ calories $\Delta T_1 \sim 16^\circ$. We thus see that the ratio $\frac{\Delta T_1}{T_0} \approx \frac{RT_0}{E}$ is always small (of the order of a few hundredths). We shall therefore in what follows, assume:

$$\frac{1}{T_0 + \Delta T_1} = \frac{1}{T_0} \left(1 - \frac{\Delta T_1}{T_0} \right) \text{ etc.}$$

Substituting the value found for T_1 in equation (3), we obtain the condition of self-ignition

$$\frac{Q v k a^n E}{N R T_0^2} \left(1 - 2 \frac{\Delta T_1}{T_0}\right) e^{-\frac{E}{R T_0} \left(1 - \frac{\Delta T_1}{T_0}\right)} = \chi S$$

or setting $\frac{\Delta T_1}{T_0} = \frac{R T_0}{E}$ and neglecting on the left $2 \frac{\Delta T_1}{T_0}$ in comparison with unity (which corresponds to an error in the value of a less than 10 percent), we obtain the condition for self-ignition in the form

$$\frac{Q v k a^n E}{N R T_0^2 \chi S} e^{-\frac{E}{R T_0}} = 1 \quad (6)$$

The number of molecules a per unit volume is connected with the pressure expressed in millimeters of mercury by the following relation:

$$p = \frac{a R T}{N} \text{ dyn/cm}^2 = \frac{a R T}{N} 10^{-6} \text{ bar/cm}^2 \\ = \frac{a R T}{N} 10^{-6} \times 750 \text{ mm Hg/cm}^2$$

where $R = 83.15 \times 10^6$ ergs. Hence,

$$p = a T 10^{19}, \quad a = \frac{p}{T} 10^{19} \quad (7)$$

Substituting in (6) we obtain a relation between the pressure p of the gas and the temperature of self-ignition

$$\frac{Q v k p^n E e 10^{19n}}{N R T_0^{2+n} \chi S} e^{-\frac{E}{R T_0}} = 1 \\ \lg \frac{p}{T^{1+\frac{2}{n}}} = \frac{A}{T_0} + B, \quad \text{where } A = \frac{0.217E}{n} \quad (8) \\ B = \frac{1}{n} \lg b, \quad b = \frac{N R \chi S}{Q v k e E 10^{19}}$$

$$\text{For } n = 1 \quad \lg \frac{p}{T^3} = \frac{A}{T_0} + B, \quad \text{where } A = 0.217 E \quad (9)$$

$$\text{For } n = 2 \quad \lg \frac{p}{T^2} = \frac{A}{T_0} + B, \quad \text{where } A = 0.11 E \quad (10)$$

In the case of a bimolecular reaction between two components of the compound - for example, hydrogen and chlorine - all formulas remain the same except that the magnitude a (the number of H_2 and Cl_2 molecules in 1 cm^3) is multiplied by the product $\gamma (1 - \gamma)$ where γ and $1 - \gamma$ are the fractions of the two components, respectively. Moreover, the heat conductivity will change with change in composition of the compound.

We shall give some examples confirming the above equation. Figure 5 shows the results obtained by Zagulin (reference 6) for the decomposition of Cl_2O , $\lg p/T$, where p_1 is the pressure at which self-ignition occurs, being plotted against $1/T$, the reciprocal of the absolute temperature of the apparatus. (Zagulin plotted as ordinates $\lg p/T$ and not $\lg p/T^2$. However, as is easy to show, in the temperature interval considered the curve $\lg p/T^2$ as a function of $1/T$ is practically a straight line which, to a first approximation, is parallel to the straight line $\lg \left(\frac{p}{T} \right)$ against $\frac{1}{T}$.)

The decomposition of Cl_2O , according to Hinshelwood (reference 7), is bimolecular where $E = 21,000 - 22,000$ calories. Zagulin obtained for A (see formula (9)) the value 2500. According to the theory and results of Hinshelwood A should be equal to 0.11 , $E = 0.11 \times 22,000 = 2400$, in good agreement with experiment.

Figure 6 gives the results of the same author (reference 6) for the self-ignition of a mixture of hydrogen with chlorine for various percentages of the components. As might have been expected, $\lg p/T$ and hence with sufficient accuracy also $\lg p/T^2$, varies linearly with the reciprocal of the absolute temperature, all of the straight lines being parallel to one another, that is, corresponding to the same value of the constant A . The latter was found to equal 2600 to 2900.

On investigating the kinetics of the reaction $H_2 + Cl_2$ for the temperature 205° , Piele showed that the reaction was bimolecular (velocity proportional to the product $[H_2] [Cl_2]$). In this case, from the data of Zagulin, we obtain $A = 0.11 E$ or $E = 2750/0.11 = 25,000$ calories.

Christiansen gives for the energy of activation of this reaction the value 25,000 to 30,000 calories. From the data of Piele (reference 8), the result obtained is that the activation energy is equal to 20,000 to 25,000 calories. On figure 7 is given the curve of $\lg p/T^3$ against $1/T$ for the self-ignition of azomethane according to Rice and Allen (reference 9). Curve 1 is for pure azomethane, and curve 2 for azomethane diluted with helium (76 percent He in mixture). The decomposition of azomethane is monomolecular. With increase in the pressure, however, the velocity constant increases somewhat, tending toward the limit k_∞ for sufficiently high pressures. For this reason, it is necessary to multiply the expression for the critical pressure by k/k_∞ and to plot not $\lg p/T_0^3$, but $\lg kp/k_\infty T_0^3$, as was done in figure 7.

The dots on the figure correspond to the tests with pure azomethane, the small crosses to the solution of azomethane and helium (He 76 percent), and the circles to the mixture with nitrogen (50 percent). The constant A was found to be 11,000. Computing E from $E = A/0.217$, the authors obtained 50,000 calories - that is, the same value (51,000) as that given by Rice and Ramsberger (reference 10) from direct kinetic tests.

As we have seen, there enter into the equation of self-ignition (formula (6)) both the parameters determining the velocity of the reaction (constant k , activation energy E) and the thermal magnitudes (heat of reaction Q , conductivity χ , dimensions of the vessel). The equation may be recast into a more simple form if these parameters are grouped in the proper manner and converted into magnitudes easily determined from tests (Todes, references 4 and 11). As one of these parameters determining the heat conduction, we shall choose the time constant of the reaction - that is, the time t_e , during which the initially heated (but not reacting) gas, due to heat conduction at the walls, decreases in temperature by e times the temperature difference ($\Delta T = T - T_0$). The time t_e does not naturally depend either on the magnitude of ΔT or on the absolute temperature T_0 because the coefficient χ does not depend on these. It can easily be shown that

$$t_e = \frac{C a v}{\chi S N} \quad (11)$$

where C is the gram molecular heat capacity.

We shall characterize the reaction velocity by a magnitude inversely proportional to it, namely, the time of the reaction t_r , denoting by the latter the time during which all the initial substance would have been consumed by the reaction if the latter occurred at a constant velocity, namely, that which corresponds to the initial concentration of the heated gas, that is,

$$t_r = \frac{a}{k a^n e^{-\frac{E}{RT}}} \quad (12)$$

the value of t_r can readily be measured. For this purpose it is sufficient to observe the initial velocity of the reaction for a temperature not far from the self-ignition point, extrapolate the value obtained to the ignition temperature, and determine t_r by dividing the total number of molecules of the initial substance per unit volume by the measured initial velocity of the reaction expressed by the number of molecules of the product formed per second.

It is easily shown that in this case formula (6) assumes the following simple form:

$$\frac{t_e}{t_r} \frac{Q E e}{C R T_0^2} = 1$$

or

$$\frac{t_r}{t_e} = \frac{Q E e}{C R T_0^2} \quad (13)$$

*We have:

$$\frac{v a C}{N} \frac{dT}{dt} = - \chi S (T - T_0)$$

Let T_1 be the initial temperature of the gas. Then

$$\ln \frac{T - T_0}{T_1 - T_0} = - \frac{\chi S N t}{C a v}$$

or

$$T - T_0 = (T_1 - T_0) e^{-\frac{\chi S N t}{C a v}}$$

hence

$$t_e = \frac{C a v}{\chi S N}$$

If $\frac{t_r}{t_e} > \frac{Q E e}{C R T_0^2}$ thermal self-ignition is impossible and a stationary reaction takes place; if $\frac{t_r}{t_e} < \frac{Q E e}{C R T_0^2}$ thermal self-ignition always occurs.

We shall now consider in greater detail the question of heat transfer to the walls of the vessel. In setting $q_2 = X (T - T_0) S$, we assumed that the heat is transferred by convection. In this case the computation of X is very difficult. There are, however, a number of tests on heat transfer, from which it can be concluded that at gas pressures less than atmospheric and for the small dimensions of the vessel such as are generally employed in self-ignition tests; and finally, for small values of ΔT_1 , the pre-explosion heating, the heat transfer process is very nearly that of conduction. Frank-Kamenetsky was the first to consider this matter and introduced into the theory of thermal self-ignition, heat transfer by conduction instead of by convection. We shall here give an approximate derivation, referring those interested in the details of the solution of the problem to the article by Frank-Kamenetsky (reference 8). Our approximation will consist in the assumption that, although in the case of heat transfer by conduction the temperature of the gas will vary at different points inside the vessel, the velocity is the same at each point and corresponds to the temperature T_1 - the mean between the maximum temperature at the center of the vessel T_{max} and the temperature T_0 at the walls. Since the pre-explosion heating is not large, this assumption leads to approximately correct results. Let us consider, for simplicity, a vessel of infinite extent whose plane walls parallel to each other at the distance $2r$ are at temperature T_0 . Inside the vessel the reaction occurs with heat liberation per second per unit volume of amount u , which is the same for all points of the space between the planes (as required by the above-mentioned assumption). We shall take the x -axis perpendicular to the walls of the vessel and for $x = 0$, we shall take the plane passing through the center between the two walls. In this case we can write down the differential equation of the heat conduction

$$\lambda \frac{d^2 T}{dx^2} + u = 0$$

which, for the initial conditions $T_{x=+r} = T_{x=-r} = T_0$

and $\frac{dT}{dx} = 0$ for $x = 0$, enables the temperature distribution to be found inside the vessel. The solution of the equation is

$$T - T_0 = \frac{1}{2} \frac{u}{\lambda} r^2 \left(1 - \frac{x^2}{r^2} \right)$$

At the center of the vessel the temperature T will be

$$T_{\max} - T_0 = \frac{1}{2} \frac{u}{\lambda} r^2$$

The flow of heat through the surface S of the vessel will be

$$q_s = - \lambda \left(\frac{dT}{dx} \right)_r S = urS$$

or, expressing u in terms of $T_{\max} - T_0$,

$$q_s = \frac{2\lambda}{r} S (T_{\max} - T_0)$$

Substituting for T_{\max} the mean value $T_1 = \frac{T_{\max} + T_0}{2}$ or $T_{\max} = 2T_1 - T_0$, we obtain

$$q_s = \frac{4\lambda}{r} S (T_1 - T_0) = \chi S (T_1 - T_0)$$

Thus $\chi = 4\lambda/r$, whence it is clear that the solution is the same as it would be for the case of heat transfer by convection except that for χ there must be substituted $4\lambda/r$. In the case of the plane-walled vessel $v/S = 2r$. Substituting χ and v/S in expression (6), we obtain the condition for self-ignition in a plane-walled vessel in the form

$$\delta_{cr} = \frac{Qka^n e^{\frac{E}{RT_0}} 2r^2}{NRT_0^2 4\lambda} = 1$$

or

$$\delta_{cr} = \frac{Er^2 Qka^n e^{\frac{E}{RT_0}}}{RT_0^2 \lambda N} = \frac{2}{e} = 0.74 \quad (14)$$

If the computation is more rigorously carried out, taking into account the variations in the velocity of reaction at various points inside the vessel then, as shown by Frank-Kamenetsky, the critical condition of self-ignition for plane-walled vessels will be

$$\delta_{cr} = 0.88 \quad (15)$$

Similarly, for a cylindrical vessel

$$\delta_{cr} = 2.00 \quad (16)$$

and for a spherical vessel

$$\delta_{cr} = 3.32 \quad (17)$$

where r in the expression for δ_{cr} is the radius of the cylinder or sphere. These expressions permit the computation of the absolute values of the self-ignition temperatures from the thermal and kinetic data. Unfortunately, there are very few reactions leading to self-ignition for which the kinetics of the corresponding reactions are accurately known.

The temperature of self-ignition of azomethane for various pressures was computed by Frank-Kamenetsky from the kinetic data, the heat of the reaction and the dimensions of the vessels used. Taking $\lambda = 10^{-4} \text{ g}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$, the compared the values computed by formula (17) with the self-ignition temperatures observed by Rice and Allen (reference 9). The same comparison was made for the decomposition of methyl nitrate (likewise a monomolecular reaction) according to the data of Appin and Chariton (reference 13), the results given below being obtained.

As may be seen, the agreement between the theoretical and the experimental values is quite good, a fact which evidently shows the correctness of the assumption of Frank-Kamenetsky as to the heat transfer by conduction in the pre-explosion range.*

On the basis of the results of Volmer (reference 14) on the kinetic decomposition of nitrous oxide, Frank-

*According to more recent values of the constant k for the decomposition of azomethane, the agreement of the theoretical with the experimental values for this reaction is somewhat less favorable.

Kamenetsky computed that this gas is subject to self-ignition at very high temperatures.

Zeldovich and Yakovlev (reference 15) actually demonstrated the self-ignition of N_2O , the observed and computed temperatures of self-ignition being found to be in very good agreement. (See table.)

Decomposition of azomethane $(CH_3)_2N_2 = C_2H_6 + N_2$ (data of Rice)			Decomposition of methyl nitrate $2CH_3ONO_2 = CH_3OH + CH_2O + 2NO_2$ (Appin and Charlton)			Decomposition of nitrous oxide N_2O (data of Zeldovich and Yakovlev)		
p mm	T° K computed	T° K observed	p mm	T° K computed	T° K observed	p mm	T° K computed	T° K observed
191	619	614	4.2	590	597	170	1255	1285
102	629	620	8.5	578	567	330	1175	1195
67	635	626	16.5	566	546	590	1110	1100
55	638	630	45.4	551	529			
38	644	636	87	541	522			
31	647	643	107	538	521			
23.5	653	651	163	531	519			
18	656	659						

We shall here consider another question relating to the absolute values of the self-ignition temperature for the cases of decomposition of Cl_2O and the reaction $H_2 + Cl_2$.

The decomposition of Cl_2O is not a simple bimolecular reaction. It is expressed most nearly by the autocatalytic law

$$w = kx(a - x)e^{-\frac{E}{RT}}$$

where a is the number of initial molecules and x is the number of reacting molecules. The reaction speed at

attains its maximum for $x = a/2$, for which $w_{\max} = k\frac{a^2}{4}e^{-\frac{E}{RT}}$. Thus the minimum self-ignition temperature is determined not by the initial speed of the process but by the maximum.

As we have seen, the maximum speed in this case varies according to the bimolecular process. This is in agreement with the results of Hinshelwood (reference 7). As we have already shown, the activation energy E , according to Hinshelwood, is 22,000 calories and the constant k is simply the constant of the bimolecular process, where $k = \sqrt{2\pi} \sigma^2 u$. According to Hinshelwood, $\sigma = 4.8 \times 10^{-8}$, $k \sim 10^{-10}$. Thus in formula (16) it is necessary to substitute $k = 10^{-10}$. In place of a we must take $a/2$ and $n = 2$. The heat of decomposition of Cl_2O is $Q = 22,000$ calories; λ may be taken approximately equal to 5×10^{-5} .

In his tests on the self-ignition of Cl_2O , Zagulin used a cylindrical vessel of radius $r \sim 1$ centimeter. According to formula (16), applied to a cylindrical vessel, we obtain

$$\delta_{cr} = \frac{E r^2 Q k a^n e^{-\frac{E}{RT}}}{R T_0 \lambda N} = 2$$

hence for Cl_2O , we shall have

$$\delta_{cr} = \frac{2.3 \times 10^4 \times 2.2 \times 10^4 \times 10^{-10} a^2 e^{-\frac{22000}{T_0}}}{4 \times 2 T_0^2 \times 5 \times 10^{-5} \times 6 \times 10^{23}} = 2 \quad (18)$$

Since we have already found that the temperature dependence of the critical self-ignition pressure of Cl_2O is in good agreement with kinetic data, it is sufficient for us to show that one of the values of the critical pressure corresponding to any ignition temperature satisfies condition (18). In this way it will be shown that the absolute values of all the test results on self-ignition may be computed from the kinetic data. We shall take one of the points obtained by Zagulin (reference 6): for $T = 454^\circ$ or $\frac{1}{T} = 22 \times 10^{-4}$, the critical self-ignition pressure is found to equal 250 millimeters of mercury. The number of molecules per unit volume is therefore:

$$a = \frac{2.7 \times 10^{19} \times 250 \times 273}{760 \times 454} = 5.4 \times 10^{18}$$

$$e^{-\frac{11000}{T}} = e^{-\frac{11000}{454}} = e^{-24.2} = 10^{-10.5} = 3.2 \times 10^{-11}$$

hence $\delta_{cr} \approx 1$. The latter value practically agrees with the value 2 since an error in T of 10° to 15° is sufficient to compensate for this difference. Moreover, a small inaccuracy in the magnitude E or an error of two times in the constant k or in the heat conduction coefficient λ can lead to the same deviation.

We shall now analyze the reaction $H_2 + Cl_2$, assuming that it follows the simple bimolecular process. According to the results of Zagulin (reference 6), $A = 2750$; that is, $E = \frac{A}{0.11} = 25,000$ calories. Since we here deal with the impact of two kinds of molecules, the total number of impacts between the H_2 and Cl_2 molecules per second per cubic centimeter will be

$$Z_{12} = 2(H_2)(Cl_2) \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \left\{ \frac{2\pi kT (m_1 + m_2)}{m_1 m_2} \right\}^{\frac{1}{2}} \quad (19)$$

If m_1 is the mass of H_2 and m_2 , the mass of Cl_2 , then $m_2 \gg m_1$ and

$$\begin{aligned} Z_{12} &= 2(H_2)(Cl_2) \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \left(\frac{2\pi kT}{m_1} \right)^{\frac{1}{2}} \\ &= (H_2)(Cl_2) \left(\frac{\sigma_1 + \sigma_2}{2} \right)^2 \left\{ \frac{2\pi RT}{\mu_1} \right\}^{\frac{1}{2}} \end{aligned}$$

Substituting $R = 83.15 \times 10^6$, μ_1 (the molecular weight of H_2), 2, $\sigma_1 = 2.4 \times 10^{-8}$, $\sigma_2 = 5 \times 10^{-8}$, and $T = 556^\circ K$, we obtain $Z_{12} = (H_2)(Cl_2) \times 7 \times 10^{-10}$. The velocity of reaction is then

$$w = 7 \times 10^{-10} (H_2)(Cl_2) e^{-\frac{25000}{RT}}$$

which for $T = 556^\circ$, gives:

$$w = 7 \times 10^{-10} (H_2)(Cl_2) \times 4 \times 10^{-10} = 2.8 \times 10^{-19} (H_2)(Cl_2)$$

According to the results of Zagulin for $T = 556^\circ$, the explosion pressure is 200 mm (100 mm H_2 and 100 mm Cl_2):

$$(H_2) = (Cl_2) = \frac{2.7 \times 10^{19} \times 100 \times 273}{760 \times 556} = 1.8 \times 10^{18} \text{ molecules in 1 cubic centimeter.}$$

$$Q = 2.2 \times 10^4$$

$$\lambda = 3 \times 10^{-4}^*$$

hence

$$\delta_{cr} = \frac{2.5 \times 10^4 \times 2.2 \times 10^4 \times 2.8 \times 10^{-19} \times 3.2 \times 10^{36}}{2.3 \times 10^5 \times 3 \times 10^{-4} \times 6 \times 10^{23}} = 4.5$$

which is a value of the same order of magnitude as the value 2 required by the heat theory. In order that 2 might be obtained instead of 4.5, it would be necessary to place the ignition temperature not at 564° but at 540°.

The reaction $H_2 + Cl_2$ is far from being a simple bimolecular reaction. Both by analogy with the photochemical reaction $H_2 + Cl_2$ at room temperature and in connection with the finding of a strong effect of oxygen traces on the thermal reaction, it is necessary to consider this as a chain reaction. The kinetics of this reaction has been but little investigated but judging by the detailed work of Piece (reference 8), the reaction formally follows the bimolecular law. Using directly the data of Piece, setting $E = 25,000$ calories, we obtain on computing δ_{cr} a value 5 to 100 times smaller than 2. This in itself would not be at all surprising but we cannot use the data of Piece because on extrapolating the straight line of Zagulin to the temperature 250°, which is the one used by Piece, we obtain the result that at this temperature the explosion should occur at a pressure equal to 500-550 millimeters, whereas Piece, at these temperatures, obtained velocity curves without any explosion at 760-millimeter pressure. Thus the reaction velocity of $H_2 + Cl_2$ of Piece was several times slower than that of Zagulin, as is entirely possible since Piece showed that there is a large variation in the velocity on varying, for example, the oxygen traces in the mixture.

* For atmospheric pressures from direct tests and the tests of Ishikawa (reference 16), it is found that the coefficient of heat conductivity $\chi = 5 \times 10^{-4} = 4\lambda/r$, $\lambda = 1.25 r \times 10^{-4}$. With increasing temperature up to 250° λ , that is, $\lambda = 3 \times 10^{-4}$, gives the correct magnitude. Moreover, we obtain this value if we set $\lambda_{H_2+Cl_2}$ equal to $\frac{1}{2} \lambda_{H_2}$.

It is assumed by Piece that the thermal reaction $H_2 + Cl_2$ is a chain process proceeding according to the following scheme:

- 1) $Cl_2 + \text{wall} \rightarrow Cl + [Cl]$ (absorbed $[Cl]$ will react on the wall with H_2 or the material of the wall)
- 2) $Cl + H_2 = HCl + H$
- 3) $H + Cl_2 = HCl + Cl$
- 4) $Cl + \text{wall} \rightarrow [Cl]$

The reaction velocity according to this scheme is $w = \frac{2k_1 k_2}{k_4} (H_2) (Cl_2)$, $k_2 = k_{20} e^{-\frac{6000}{RT}}$, where k_{20} practically agrees numerically with the value $k_1 = k_{10} e^{-\frac{E}{RT}}$ computed by formula (19); k_4 does not depend on the temperature.

Taking $E = 31,000$ calories and $2k_{10}/k_4$ of the order of 1 (which is very likely if both magnitudes are equal to $uS/4v$ where u corresponds to the thermal speeds with which the Cl_2 molecules and Cl atoms strike the wall, respectively), we formally arrive at the same simple bimolecular law on which we based our computation of the absolute values of the ignition temperature and compared with the test values.

Besides the above numerical computations, a large number of qualitative facts is found to be in agreement with the thermal theory. Thus the mixing of azomethane with nitrogen changes only slightly the critical self-ignition pressure in correspondence with the fact that the heat conductivity of nitrogen is approximately that of azomethane. On the other hand, the addition of helium very greatly increases the critical pressure of the azomethane because of the higher heat conductivity of helium. For the case of the reaction $H_2 + Cl_2$, it was shown by Zagulin (reference 6) that the minimum critical pressure on varying the components of the mixture is at about 70 percent Cl_2 . This at first glance contradicts the bimolecular reaction. If we take into account, however, the fact that the heat conductivity of Cl_2 is much less than that of H_2 , then it is understandable that the self-ignition is decreased with increase in percent Cl_2 . On increasing the dimensions of the vessel,

the critical self-ignition pressure drops as may be expected from the theory.

The self-ignition condition, expressed in the form $\frac{t_r}{t_e} = \frac{Q E e}{C R T_0}$ (see formula (13)) to a sufficient degree of accuracy is also applicable to the conductive process of heat transfer. In order to show this it is necessary to compute the reaction times for plane, cylindrical, and spherical vessels. It is here necessary to solve the cooling equation of a heated gas $\frac{\partial T}{\partial t} = \frac{\lambda}{c} \Delta T$, where $\Delta T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$ (λ is the heat conductivity and c is the specific heat of a unit volume of the gas). The solution of this equation for the three cases is obtained in form of a series - each term of which contains $e^{\rho_1 t}$, where ρ_1 is a magnitude rapidly increasing with increase in i . The time t_e will therefore be approximately $1/\rho_1$ where ρ_1 is the first and smallest of all the ρ_i . A well-known computation (reference 17) gives for the vessel with plane walls separated at distance $2r$

$$t_e = \frac{4cr^2}{\lambda \pi^2} = \frac{cr^2}{2.6 \lambda} \quad (20)$$

For the cylindrical vessel of radius r

$$t_e = \frac{4cr^2}{\lambda \pi^2} = \frac{cr^2}{5.7 \lambda} \quad (21)$$

and for the spherical vessel of radius r

$$t_e = \frac{cr^2}{10 \lambda} \quad (22)^*$$

Remembering that $t = \frac{a}{k a^n e^{-\frac{E}{RT}}}$ and substituting t_e and t_r in condition (13), we obtain:

*The specific heat of a unit volume of the gas c is connected with the specific heat of a gram molecule C by the relation $\frac{c}{a} N = C$.

$$\delta_{cr} = \frac{r^2 k a n_e - \frac{E}{RT_{Qe}}}{NRT_0^2 \lambda}$$

for the cylindrical vessel $\delta_{cr} = 2.1$ (instead of 2, computed by Frank-Kamenetsky); for the spherical vessel $\delta_{cr} = 3.7$ (instead of 3.32, computed by Frank-Kamenetsky). (See formulas (16) and (17).)

Thus we may say that condition (13) is actually valid also for the case of heat transfer by conduction for any shape vessel.

Relation (13) is of great importance in determining the nature of the self-ignition process. In addition to thermal self-ignition, there are cases of self-ignition determined by an isothermal acceleration of the chemical process (chain ignition). It is not always easy to separate the one process from the other and expression (13) provides a good method for this purpose.

Thus if the reaction time measured directly at the ignition point or extrapolated for it

$$t_r \leq \frac{Q E e}{CRT_0^2} t_e \quad (23)$$

then the ignition is of a thermal nature. If, however,

$$t_r > \frac{Q E e}{CRT_0^2} t_e \quad (24)$$

and especially, if it is very much larger than this magnitude, we may state with assurance that we are not dealing with thermal ignition but with a process of a different nature.*

We shall illustrate the application of formula (13) with a few examples. Let us consider whether the reaction

*In computing t_e we assumed the heat transfer to be conductive. If, however, it is actually convective, the true value of t_e will be less than the value of t_e in the formula. Thus if we conclude that thermal explosion is impossible at the computed value of t_e (inequality (24)), then it is all the more impossible if the true t_e is still smaller.

$H_2 + Cl_2$ occurring under illumination of a light source of great intensity leads to a thermal explosion. We shall make the computation for a cylindrical vessel of radius $r = 1$ illuminated by a light source and filled with an equimolecular mixture $H_2 + Cl_2$. We know that each quantum of light absorbed (in the portion of the spectrum from blue to deep ultraviolet) gives rise to a reaction chain of from 10^3 to 10^6 molecules of HCl in length. Under conditions where the H_2 and Cl_2 are not especially purified, no fewer than 10^3 molecules of HCl appear from the absorption of one quantum. If n_0 is the number of light quanta absorbed per unit volume $w = 10^3 n_0$ or $t_r = a/w$

$$= \frac{10^{19}}{n_0 \cdot 10^3} = \frac{10^{16}}{n_0}.$$

For a cylindrical vessel (taking $\lambda_{H_2+Cl_2} = 10^{-4}$ and the specific heat of a unit volume $c = \frac{5}{2 \times 10^4}$

$$t_e = \frac{cr^2}{5.7 \lambda} = \frac{5}{5.7 \times 2 \times 10^4 \times 10^{-4}} \sim 0.5 \text{ sec}$$

The activation energy E for the photochemical reaction is well known and is equal to 6000 calories; $Q = 22,000$ calories. For self-ignition, it is necessary that

the condition $\frac{t_r}{t_e} = \frac{QEe}{CRT_0}$ be satisfied or, substituting

numerical values $\frac{10^{16}}{n_0 \cdot 0.5} = \frac{2.2 \times 10^4 \times 6 \times 10^3 \times 2.7}{5 \times 2 (300)^2}$ whence $n_0 = 5 \times 10^{13}$ quanta absorbed per second per cubic centimeter.

The photochemical self-ignition of $H_2 + Cl_2$ occurs approximately at these light intensities. Hence in this case the self-ignition is thermal in character.

As another example, let us take the case of the displacement of the self-ignition limit of an explosive compound under the action of ultraviolet light. Plotting the pressure against the temperature, the self-ignition region of an explosive mixture is found to have a peculiar character entirely different from the cases considered above. (See fig. 8.) Together with a lower limiting pressure, there is an upper limiting pressure, above which

no ignition occurs at the given temperature. A large number of oxidation reactions and some decomposition reactions possess this property. A reaction velocity slightly below the lower limit and slightly above the upper limit is sufficient for relation (13) not to be satisfied. We are thus here confronted with an ignition process which is not of a thermal character. These cases of chain reactions are fully described by the chain-reaction theory and lie outside the scope of our present article.

On illuminating an explosive mixture with ultraviolet light of very short-wave length (1400 to 1800 Å), a photochemical reaction occurs. The light dissociates the oxygen into atoms which start the chain reaction. According to Nalbandyan's results (soon to be published), which we shall make use of in what follows the length of the chain; that is, the number of molecules of water for one atom of oxygen, taken as equal to unity at room temperature, increases to two times at 350°, and thereafter begins to increase rapidly. In the range from 410° to 460°, this in-

crease takes place according to the law $e^{-\frac{E}{RT}}$, where the energy of activation $E = 30,000$ calories. This occurs in the case where the light intensity is sufficiently small. On increasing the light intensity the length of the chain - starting from a certain temperature - begins to increase more rapidly than at the small intensity, and when it reaches a certain critical value at temperature T , less than the self-ignition temperature (for a given pressure), photochemical self-ignition occurs. The greater the light intensity the lower the temperature at which the ignition occurs. The region of ignition is displaced to the left (fig. 8, curves 1, 2, 3 in succession), the displacement increasing with the intensity. There is a widely held view that this displacement is associated with thermal self-ignition occurring at large light intensities. The analysis here presented by Nalbandyan and the author shows that this is not the case.

As we know, for thermal self-ignition it is necessary that t_r/t_e should not be greater than QEe/CRT_0^2 . From the data of Nalbandyan, it is known that in the mixture $2H_2 + O_2$ at an 18-millimeter pressure and under illumination, self-ignition occurs at $T = 434^\circ C$ (i.e., at $25^\circ C$ below the value in the absence of illumination). At a temperature 1° lower (than $434^\circ C$) the measured reaction velocity corresponds to $t_r = 66.6$ seconds. The tests were

conducted in a cylindrical pipe of radius 1.12 centimeters. The specific heat of the mixture $2H_2 + O_2$ under these conditions is $c = 3 \times 10^{-6}$. The heat conduction coefficient of this mixture, according to tabulated data, is 23.73×10^{-5} at room temperature. Taking account of the increase in the conductivity with temperature, we may assume $\lambda_{4340} = 47.5 \times 10^{-5}$. According to formula (21), we then find for the time t_e

$$t_e = \frac{cr^2}{5.7\lambda} = \frac{3 \times 10^{-6} \times 1.23}{5.7 \times 47.5 \times 10^{-5}} = 1.4 \times 10^{-3} \text{ sec}$$

Thus $\frac{t_r}{t_e} = 4.7 \times 10^4$; the heat $Q = \frac{2}{3} \times 60,000 = 40,000$ whence, taking the activation energy for the photochemical reaction, $E = 30,000$ and the molecular specific heat $C = 5$,

$$\frac{Q E e}{C R T_0^2} = \frac{4.7 \times 10^4 \times 3 \times 10^4 \times 2.7}{5 \times 2 \times 5 \times 10^5} = 7.5 \times 10^2$$

Thus $\frac{Q E e}{C R T_0^2} < \frac{t_r}{t_e}$, that is, the photochemical ignition of the mixture $2H_2 + O_2$ as well as the thermal self-ignition cannot arise from any thermal cause and must have an entirely different origin.

Up to the present, we limited our analysis to the critical condition for self-ignition and said nothing as to how the temperature and quantity of reacting substances vary with the time. We now, following Todes (reference 4), briefly consider this question - first making the simplifying assumption that the reaction velocity does not change with time but remains the same as at the start. This assumption is not of course strictly true since the number of initial molecules decreases with time, but as we shall show below, the assumption does not lead to any large error in the computation. The equation determining the time rate of change of the temperature of the gas will now be

$$\frac{C_{av}}{N} \frac{dT}{dt} = \frac{k a^n e^{-\frac{E}{RT}}}{N} Q_v - \chi S (T - T_0) \quad (25)$$

At pressures below the critical this equation leads to the gradual establishment of the steady temperature $T_1' = T_0 + \Delta T$.

In the case where the pressure is considerably above the critical, the second term on the right side of the equation may be neglected and the equation

$$\frac{dT}{dt} = \frac{k a^{(n-1)} Q e^{-\frac{E}{RT}}}{C}$$

can be integrated.

The integration of the above equation gives a characteristic curve of temperature variation with time. Figure 9 shows the solution for a monomolecular reaction with constant $k = 10^{14}$, $\frac{E}{RT} = 40$, $\frac{Q}{CT_0} = 25$. As may be seen,

for a relatively large time interval (2 to 3 sec), the temperature rises very slowly until it reaches the value

$T_0 + \frac{RT_0^2}{E} \left(\frac{RT_0^2}{E} - \text{the pre-explosion heating} \right)$. Beyond

that instant, the further rise in temperature up to the value corresponding to the explosion temperature (a few thousand degrees), is practically instantaneous or, more accurately, extends over a negligible fraction of the time interval t . After the entire original product has been consumed the gas begins to cool. The curve in figure 9 is discontinuous since it is naturally impossible to lay off on the same ordinate temperatures of the order of a few degrees and a few thousand degrees. The time t_i from the start of the reaction to the pre-explosion heating is called the period of induction. It practically coincides with the time from the start of the reaction to the explosion; the latter is easily measured experimentally. For t_i , Todes found the approximate expression

$$t_i = \frac{RT_0 CT_0 a}{EQ k a^n e^{-\frac{E}{RT}}} = t_r \frac{CRT_0^2}{EQ}$$

Since $\frac{RT_0}{E}$ is a small quantity, not exceeding 0.05 for those cases of interest to us, $\frac{CT_0}{Q}$ is also a small quantity of the order of $\frac{5 \times 500}{20000} \approx 0.1$ or less, $\frac{CRT_0^2}{EQ}$ is of the order of 0.01 to 0.001. Hence $t_i = 0.01 - 0.001 t_r$

is the order of magnitude of the induction period. Recalling now the relation $t_r \leq \frac{Q E_0}{C R T_0^2} t_0$, we have $t_i \leq e t_0$.

In the neighborhood of the critical pressure t_i increases several times but remains the same order of magnitude.

The above considerations lead to a very important result. Since from the start of the reaction to the end of the induction period is 0.01 to 0.001 of the reaction time, at the instant of an abrupt rise in temperature or at the instant of explosion the time is not sufficient for more than 1 percent of the substance to undergo change. This circumstance fully justifies the assumption that the reaction velocity is practically constant up to the very instant of explosion. It furthermore justifies not only our computations of the induction period but also our previous computations of self-ignition point since we everywhere assumed that the number of reacting molecules at the instant corresponding to the point of tangency of the heat conduction straight line with the curve of heat liberation remains the same as in the initial gas. For this reason, any more complicated consideration as to the explosion conditions becomes unnecessary for those cases of interest to us.

The case is very different where the reactions are associated with small values for E or Q , where we no longer have the typical explosive process. If the activation energy is very small and the reaction occurs for each impact of the particles, it is not possible in general to prepare such a gas for if we have a reaction between two gases we cannot mix them. They will burn at the separation boundary on mixing. This is the case, for example, in mixing sodium vapor with chlorine. If the activation energy is small but the reaction velocity is not too great, the heating ΔT will be very large and there will be no quantitative difference between reactions occurring below or above the explosion limit.

At small values of E the absence of a sharp boundary between the steady and explosive states is associated with a large increment ΔT and means that even at a large velocity the reaction is still in the steady state. In the case of small values of Q , on the other hand, the absence of the sharp boundary is due to the fact that high temperatures correspond to the explosion conditions, so that the reaction velocity is high up to the attainment of these temperatures.

We should therefore consider as typical explosive gases, those which possess simultaneously a high value of Q (20,000 or more cal/mol) and a high thermal stability against decomposition - that is, a high energy of activation E (20,000 cal or more). All the results obtained by us are applicable in practice to these typical explosive gases. It is necessary to note, moreover, that a small value of E makes the explosion nontypical only in the case where the velocity of the monomolecular or bimolecular reaction is associated with an abnormally small constant k . When this is not the case (when, for example, for a bimolecular reaction $k = \sqrt{2\pi\sigma^2 u}$) the small value of the activation energy does not prevent any sharpness in the explosive conditions and does not mask the explosion phenomenon. The difference is only that the explosion occurs at very low temperatures. The value E/RT remains large in spite of the relatively low value of E .

To the above cases belongs, apparently, the explosion of HBr with ozone, which reaction is quite sharply defined but occurs at a temperature of the order of 100°C , or the explosion of H_2 with fluorine. For the case of a small value of Q with normal E , the distinction between the explosive and the stationary reactions becomes less sharp. In the work of Todes and Melentyev (reference 4) an accurate analysis (by numerical integration) is made of the character of the phenomenon for monomolecular reactions (with the constant $k = 10^{13}$).

We present two curves showing how the reacting substance changes with time ($t = \frac{b}{a}$, where b is the number of reacting molecules and a the initial): 1) case of large Q (typical explosion, fig. 10), and 2) case of small Q (fig. 11). These curves well illustrate the above qualitative considerations. Figure 12 shows the variation of the temperature with the time corresponding to the same conditions as for figure 10 (typical explosion). We see that for a typical explosion a change in pressure of 0.2 percent near the self-ignition limit qualitatively changes the picture of the process.* Nothing similar is

*Here $\mu = \chi S/C_{av}$, that is, inversely proportional to the pressure p . We see that for large Q on changing μ from 6.84×10^4 to 6.83×10^4 , i.e., on changing the pressure by 0.14 percent, there is a sharp change in the picture of the combustion process. For μ equal to 6.83×10^4 , the reaction is slow, while for a value 6.84×10^4 after a certain induction period the rate is several times multiplied (explosion).

observed in the case of small Q (fig. 11; figures at curves give the values of μ).

With the above we conclude the theory of thermal self-ignition for simple reactions and pass on to the consideration of problems connected with thermal explosion for autocatalytic processes.

It has been shown that for pressures beyond the critical the induction period is generally very small and is measured in times of the order of 1 second. In many cases, however, the self-ignition occurs with a considerably larger lag period. Thus, for example, the self-ignition of a mixture of methane with oxygen at a temperature of 730°C and pressure of 40 millimeters occurs with a lag of 4 minutes. The same order of magnitude of induction period is observed for other hydrocarbons and the oxidation of carbon sulphide, hydrogen sulphide, and the decomposition of Cl_2O . Particularly large ignition delays are observed with liquid and solid explosive materials often measured in 10's of minutes and even hours. According to the results of Roginsky and his coworkers (reference 18) on the explosion of trinitrotoluene and nitroglycerine in closed flasks, the ignition lags sometimes reach 5 to 10 hours.

A study of the kinetics of these reactions* shows that they are all autocatalytic, that is, the reaction velocity as a function of the quantity of reacting substance x in the first stages of the chemical change, is described by the equation $\frac{dx}{dt} = \phi x + n_0$ where n_0 is the number of molecules of the final or intermediate product produced per second per unit volume. These may be produced as a result of bimolecular or monomolecular reactions or as a result of a heterogeneous process. In the majority of cases n_0 is very small and may be neglected for large values of ϕ . If, however, we wish to express x or w as a function of the time, then it is necessary to know n_0 since the integration of the equation gives

$$x = \frac{n_0}{\phi} (e^{\phi t} - 1) \quad \text{and} \quad \frac{dx}{dt} = n_0 e^{\phi t} \quad (26)$$

The constant ϕ itself decreases as the reaction progresses, due to the decrease in the quantity of initial

*The theory of these phenomena was developed at the Institute of Chemical Physics. For bibliography, see reference 3.

substances. In a particular case $\varphi = \varphi_0 (a - x)$. Here the reaction velocity as a function of x is shown in figure 13, and as a function of the time by the curves of figure 14, where 1, 2, 3, 4 correspond to the pressures $p_1 > p_2 > p_3 > p_4$.

If, for the occurrence of thermal explosion, it is necessary that the reaction velocity should reach a certain critical value w_{cr} , then at pressure p_1 the explosion occurs after time τ_1 , for pressure p_2 after time τ_2 ; for pressure p_4 the explosion will in general not occur. The minimum pressure at which explosion is possible will be p_3 , and this pressure corresponds to the maximum possible lag τ_3 . Thus in these cases the induction period is connected, not with the heating of the mixture, but with the time necessary for the isothermal reaction to proceed up to a point where an explosion is possible. For this reason the induction period can be greatly prolonged.

We shall now express mathematically the self-ignition conditions for a given case, limiting ourselves to the first stages of the reaction (10 to 20 percent), for which we may assume φ as a constant depending on the quantities of initial substances and on the temperature. Generally the constant φ is proportional to the first or second power of the pressure of the mixture or, what amounts to the same thing, to the number of molecules of the initial substances per unit volume, and increases exponentially with

the temperature according to the law $e^{-\frac{E}{RT}}$. We limit ourselves further to those cases for which the time constant t_0 (of the order 0.01 to 0.5 sec) is small in comparison with the time of autocatalytic acceleration of the reaction, and may be neglected. Under these assumptions the entire theory developed above remains valid except that in place of $w = k a^n e^{-\frac{E}{RT}}$, we must have in the formula

$$w = f a^n x e^{-\frac{E}{RT}} + n_0 = \varphi x + n_0$$

Thus, for example, on the assumption of conductive heat transfer for a cylindrical vessel, the critical condition (formula (16)) for self-ignition will be

$$\delta_{cr} = \frac{E r^2 Q (\varphi x + n_0)}{R T_0^2 \Delta N} = 2 \quad (27)$$

From the above equation, knowing n_0 and $\phi = f a^{n_0} e^{-\frac{E}{RT}}$, we may compute x , that is, the extent of the chemical change before explosion occurs. A magnitude generally of greater interest is the lag interval, which is easily measured experimentally. As we have seen, $x = \frac{n_0}{\phi} (e^{\phi \tau} - 1)$. Substituting this expression in formula (27), we obtain:

$$n_0 (e^{\phi \tau} - 1) + n_0 = n_0 e^{\phi \tau} = \frac{2RT_0^2}{E r^2 Q} \lambda N \quad (27)$$

where τ is the lag before explosion occurs; whence

$$0.434 \phi \tau + \lg \frac{n_0}{T_0^2} = \lg \frac{2R\lambda N}{E r^2 Q} = \text{const} \quad (28)$$

since we neglect the weak dependence of λ on the pressure and temperature.

The magnitude $\frac{2R\lambda N}{E r^2 Q} \approx \frac{10^{-5} \times 10^{23}}{10^4 \times 10^4} \approx 10^{10}$ whence the constant ≈ 10 . In the case of small n_0 , for example, less than 10^3 , $\lg \frac{n_0}{T_0^2} \approx 2$. For smaller n_0 , for example 10^4 , $\lg \frac{n_0}{T_0^2} \approx -2$. We see that for a variation in n_0 by 10^4 times $0.434 \phi \tau$ varies only by 20 percent - about the value 10. Thus in this case we may assume that on changing the pressure and temperature within a sufficiently large interval,

$$\phi \tau = f a^{n_0} e^{-\frac{E}{RT}} = \text{const} \quad (29)$$

Hence for a constant pressure the relation between the lag period and the absolute temperature should satisfy the relation

$$\lg \tau = \frac{A}{T} + B \quad (30)$$

where

$$A = \frac{0.434 E}{R} \approx 0.22 E$$

At constant temperature and with change in pressure, we must have the relation

$$\lg \tau = C - n \lg p \quad (31)$$

In the case of autocatalytic decomposition of explosive materials, only the temperature may change and only relation (30) must hold. The constant here will naturally be essentially different for gases under other conditions of reaction.

Formula (30) was first established by Roginsky (reference 18) and his coworkers for trinitrotoluene and nitroglycerine in closed flasks. (The use of closed flasks is apparently necessary to prevent splashing of the autocatalytic products.) Figure 15 gives the results of Roginsky for trinitrotoluene. The energy of activation for this substance was found to be 27,000 calories, and for nitroglycerine, 25,700 calories.

After we had developed the theory of the induction period, Garner and his coworkers (reference 19) carried out a number of investigations on the decomposition of crystals of solid explosives in evacuated retorts, studying both the kinetic process and the relation between the explosion lag interval and the temperature. It was found that the law $w = n_0 e^{\varphi t} = 10^{0.434 \varphi t}$ applies with good approximation to the first stages (20 to 30 percent) of the decomposition for a number of explosive substances (lead styphnate, barium azide, mercury fulminate). It was found, on changing the temperature by 50° C, that the value of n_0 was practically constant. The value of φ varies with

the temperature according to the law $e^{-\frac{E}{RT}}$. The activation energy E is equal to 40,000-60,000 calories for lead styphnate and 30,000 calories for mercury fulminate.

The relation between $\lg \tau$ and $1/T$ was found, in agreement with the theory, to be linear - the energy of activation E , computed from the constant A for lead styphnate, being equal to 39,000 and for mercury fulminate 30,000 calories - that is, practically the same as for the magnitude φ as should also follow from the theory.

For combustible gases this type of investigation of the induction period was unfortunately carried out only

for the case of oxidation of methane at high temperatures. The oxidation of methane is an autocatalytic reaction satisfying the law $w = n_0 e^{\varphi t}$ up to 30-40 percent of the process. Formulas (30) and (31) were checked by Neiman and Yegorov (reference 20), who showed that the relation

$\text{Re } \frac{E}{RT} p^n = \text{const}$ was applicable with a large degree of accuracy. On figure 16 is shown the plot of $\lg p$ against $1/T$ experimentally obtained for various pressures of a mixture of methane with oxygen. The activation energy E is equal to 90,000 and the exponent n has nearly the value 2. Kinetic tests conducted by Bone (reference 21) and Hinshelwood (reference 22) (at much lower temperatures, however) give for the constant φ values near E .

It is here necessary to note the relation between $\lg p$ and $1/T$ for constant lag interval and the same relation applied to the minimum explosion pressure for each given temperature. In the first case (constant τ in the initial stages of the reaction)

$$\lg p = \frac{0.22E}{n T} + C = \frac{A}{T} + C \quad (32)$$

For methane $\frac{0.22E}{n} = A \approx 10,000$. In the second case the coefficient of $1/T$ is somewhat different.

In the initial stages φ increases with the number of molecules in the vessel (and hence also with the pressure) according to the law $w = \varphi x = f a^2 e^{-\frac{E}{RT}}$. When the quantity of reacting substance is large, $\varphi x =$

$f(a-x)^2 x e^{-\frac{E}{RT}}$ or $f a(a-x) x e^{-\frac{E}{RT}}$ (the latter in a case where the total pressure of the mixture is important as, for example, for chains breaking at the walls). Corresponding to these the maximum velocity of the reaction will be

$$w_m = f \frac{4}{27} a^3 e^{-\frac{E}{RT}} \quad \text{or} \quad w_m = f \frac{1}{4} a^3 e^{-\frac{E}{RT}}$$

In any case the maximum velocity will be proportional to the cube of a and hence to the cube of p . Hence by the thermal explosion formula

or, approximately, $\lg \frac{P_m}{T} = \frac{0.22E}{3T} + C'$ or, in the general case, for any value of n :

$$\lg P_m = \frac{0.22 E}{(n+1)T} + C' = \frac{A_1}{T} + C' \quad (33)$$

Thus the temperature coefficient of the minimum explosion pressure will be less than the temperature coefficient of the explosion pressure at constant lag interval (corresponding to tests with small pre-explosion heating) in the ratio $\frac{n}{n+1}$. In particular, for methane, for $n = 2$ this ratio will be $2/3$. If the value of A in formula (32) is equal to 10,000, then for the coefficient A_1 there is obtained the value $A_1 = \frac{2}{3} A \approx 6600$.

Zagulin (reference 6) experimentally determined the dependence of the minimum explosion pressure on the temperature and obtained straight lines similar to those of figures 6 and 5. From these curves he found $A_1 = 7000$, that is, a value very near the computed value 6600.

The relation $0.434 \varphi T = \text{const}$ was derived on the assumption that $\lg \frac{n_0}{T_0^2}$ was at least half $P = \ln \frac{2R\lambda N}{Er^2 Q}$. In the case that this magnitude is near the value of P and n_0 itself changes with the temperature, the relation $\varphi T = \text{const}$ ceases to be valid and it is necessary to make use of the relation $\varphi T + \ln \frac{n_0}{T_0^2} = \text{const}$ or approximately

$$0.434 \varphi T + \lg n_0 = \text{const} \approx 16 \quad (34)$$

(since n_0 is proportional to T_0 to a power higher than the second). This formula must be used when $\lg n_0$ is of the same order of magnitude as the constant, that is, $\lg n_0$ is near 16 when $0.434 \varphi T$ is considerably less than $\lg n_0$. The relation may be rewritten in the form $n_0 e^{\varphi T} = \text{const}$.

For small values of φT , corresponding to large n_0 , we obtain a second limiting expression:

$$n_0 e^{\phi T} = n_0 (1 + \phi T) = \text{const}$$

or

$$\phi T = \frac{\text{const}}{n_0} - 1$$

that is, with increasing temperature ϕT drops.

In the limit, when n_0 is very large, ϕT may in general be neglected and the explosion will occur without any lag or, more accurately, with a lag determined by t_0 .

The velocity w for $t = 0$ is equal to n_0 . If n_0 is so large that a thermal explosion is possible, there is no necessity for a self-accelerated reaction as a result of autocatalysis. This apparently is the fundamental reason for the considerable lowering in the self-ignition temperature on adding to the combustible mixture very small quantities of certain active compounds of the type NO_2 . These additions, by reacting on the combustibles, considerably raise the rate of formation of the final or active products. On increasing n_0 , the value of ϕT drops, but since for a given temperature ϕ is constant, there is a considerable decrease in the induction period. On the other hand, keeping T constant we can, by the addition of an active compound, considerably decrease ϕ , that is, lower the explosion temperature.

II. IGNITION BY MEANS OF HEATED BODIES

Before proceeding to the computation of the ignition temperature of combustible gases ignited by heated wires or small spheres, that is, bodies of dimensions such as are employed for this purpose, let us consider, following Zeldovich (report to be published) the ignition conditions for a gas contained between two parallel walls, one of which is maintained at a high temperature T_1 , and the second at a low temperature T_0 . In order to exclude convection, the plates are assumed to lie parallel to the ground, the plate at the higher temperature being at the top. The problem is that of finding the minimum temperature T_1 of the hot plate at which (with the other plate at room temperature T_0) the gas is ignited.

The reaction velocity as before will be assumed as

equal to $w = k a^n e^{-\frac{E}{RT}}$ and the quantity of heat generated per second per unit volume $\frac{Q k a^n e^{-\frac{E}{RT}}}{N}$.

On account of its exponential dependence on the temperature the reaction will take place mainly near the hot wall so that the linear drop of the temperature with distance from the upper plate will not hold true. This decrease in the temperature gradient near the hot wall will be greater the higher the temperature T_1 since the reaction will then be more energetic and more heat will be liberated. The corresponding temperature distributions for various values of T_1 are schematically shown in figure 17. It was shown rigorously by Zeldovich (and qualitatively demonstrated by van't Hoff) that ignition occurs at that temperature T_1 at which the temperature gradient $(dT/dx)_{x=0}$ near the hot surface becomes equal to zero or, otherwise expressed, at which the plate does not lose heat and all the heat flowing to the cold plate will be generated by the reaction taking place in a relatively narrow zone ξ near the hot plate.

We shall compute the quantity of heat generated at T_1 near the ignition temperature, that is, when $(dT/dx)_0 = 0$. As we shall see below, the distance ξ is about 10 percent of the distance d between the plates, and thus the gradient dT/dx for $x > \xi$ will not only be linear as before, but its magnitude also will differ from $(T_1 - T_0)/d$ by not more than 10 percent; that is, the same gradient that would be obtained for an inert, nonreacting gas between the plates. We may therefore assume that the flow of heat through 1 square centimeter at $x > \xi$ will always be approximately equal to $q = \lambda \frac{T_1 - T_0}{d}$ where λ is the conductivity for a hot gas.

The equation for determining the temperature distribution with account taken of the heat generated by the reaction is

$$\lambda \frac{d^2 T}{dx^2} + F(T) = 0 \quad (1)$$

where $F(T) = \frac{Q}{N} k a^n e^{-\frac{E}{RT}}$. Near the hot wall the difference

$T_1 - T$ is small in comparison with T_1 and we may set

$$e^{-\frac{E}{RT}} = e^{-\frac{E}{RT_1}} e^{-\frac{E(T_1-T)}{RT_1^2}} \quad \text{whence} \quad \frac{dT}{dx} = -F(T_1) e^{-\frac{E(T_1-T)}{RT_1^2}} \quad (2)$$

Integrating this equation for the condition $\left(\frac{dT}{dx}\right)_0 = 0$ (ignition condition) and $T_{x=0} = T_1$, we obtain:

$$\frac{dT}{dx} = \sqrt{\frac{2F(T_1)RT_1^2}{\lambda E} \left(1 - e^{-\frac{(T_1-T)E}{RT_1^2}}\right)} \quad (3)$$

The magnitude $\frac{RT_1^2}{E}$, as we have already seen, generally does not exceed a few tens of degrees and hence is always less than $T_1 - T_0$.

In changing $T_1 - T$ from 0 to $\frac{RT_1^2}{E}$, the variable quantity under the root sign $\left(1 - e^{-\frac{(T_1-T)E}{RT_1^2}}\right)$ varies from 0 to 0.63. With further increase of $T_1 - T$ to $\frac{2RT_1^2}{E}$, this magnitude increases almost to 0.9, and further on remains practically equal to unity.

We see that the greatest part of the increase of the gradient $\frac{dT}{dx}$ already ends at $T_1 - T = \frac{RT_1^2}{E}$, that is, that the main part of the reaction is concentrated in this zone. Further on the gradient maintains practically a constant value.

$$\frac{dT}{dx} = \sqrt{\frac{2F(T_1)RT_1^2}{\lambda E}} \quad (4)$$

In accordance with the above, we may equate this gradient to $(T_1 - T_0)/d$, whence

$$d = \sqrt{\frac{\lambda E (T_1 - T_0)^2}{2F(T_1)RT_1^2}} = \sqrt{\frac{\lambda E (T_1 - T_0) N e^{\frac{E}{RT_1}}}{2Qka^2}} \quad (5)$$

which gives the ignition condition connecting the distance between the plates and the gas pressure p with the ignition temperature T_1 .

The width of the zone ξ within which the greater part of the reaction takes place is determined by integrating equation (2) where as a first approximation

$$\sqrt{1 - e^{-\frac{(T_1 - T)E}{RT_1}}} \approx \sqrt{\frac{0.63}{2}} = \sqrt{0.30} \sim 0.5$$

We find

$$\xi = \frac{RT_1^2}{E} \frac{1}{0.5 \sqrt{\frac{2F(T_1)RT_1^2}{\lambda E}}} = \sqrt{\frac{2RT_1^2 \lambda}{EF(T_1)}} \quad (6)$$

The ratio

$$\frac{\xi}{d} = \sqrt{\frac{2RT_1^2 \lambda 2F(T_1)RT_1^2}{EF(T_1) \lambda E (T_1 - T_0)^2}} = 2 \frac{RT_1}{E} \frac{T_1}{T_1 - T_0} \quad (7)$$

is a magnitude of the order 0.1; that is, the zone within which the reaction occurs is considerably less than the distance between the plates.

We now pass on to the consideration of those cases of interest to us - that is, ignition of the gas by small heated bodies; namely, small spheres and wires. Let the sphere of radius ρ heated to temperature T_1 be placed at the center of a sphere of very large radius R ($R \gg \rho$), which is filled with the reacting gas. By assuming that the zone within which the reaction occurs extends to a distance from the surface of the sphere very much less than the radius of the sphere the problem, to an accuracy sufficient for our purposes, is reduced to the parallel plate case just considered. The ignition condition as before will be $(dT/dr)_{r=\rho} = 0$. The reaction zone will ex-

tend from the sphere surface to distance ξ which, as before, is expressed by the formula

$$\xi = \sqrt{\frac{2 RT_1^2}{EF(T_1)}}$$

The flow of heat through unit bounding surface of the reaction zone is approximately given by formula (4) since beyond the boundaries of ξ the heat from the reaction may be neglected. The integrated heat flow through the closed surface of radius $r = \rho + \xi$ will be

$$4\pi (\rho + \xi)^2 q = 4\pi (\rho + \xi)^2 \sqrt{\frac{2F(T_1) RT_1^2 \lambda}{E}} \quad (8)$$

This is equal to the flow through any other surface of the sphere of radius r .

For $r > (\rho + \xi)$ where the reaction may be neglected the temperature distribution will not be different from the temperature distribution in the nonreacting gas except that instead of the sphere of radius ρ we must take a sphere of radius $\rho + \xi$ since the temperature drop in the small reaction zone itself is negligible.

The temperature distribution about the sphere of radius $\rho + \xi$ heated to $T = T_1$ with the temperature at infinity T_0 will be

$$T - T_0 = \frac{(T_1 - T_0) (\rho + \xi)}{r}$$

and the flow

$$q = -\lambda \frac{dT}{dr} = \lambda \frac{(T_1 - T_0) (\rho + \xi)}{r^2}$$

The integrated flow through the sphere of radius r is

$$4\pi q r^2 = 4\pi (T_1 - T_0) (\rho + \xi) \lambda \quad (9)$$

Equating (8) and (9), we obtain:

$$4\pi (\rho + \xi)^2 \sqrt{\frac{2F(T_1) RT_1^2 \lambda}{E}} = 4\pi (T_1 - T_0) (\rho + \xi) \lambda$$

or

$$(\rho + \xi) = \sqrt{\frac{\lambda E(T_1 - T_0)^2}{2F(T_1)RT_1^2}} \quad (10)$$

The ratio $\frac{\xi}{(\rho + \xi)} = \frac{2RT_0^2}{E(T_1 - T_0)}$ is less than unity. Let us take, for example, $T_1 = 600^\circ \text{C}$, $T_0 = 300^\circ \text{C}$, $E = 30,000$, then $\frac{\xi}{(\rho + \xi)} = \frac{1}{6}$. Thus we have shown that our assumptions of the smallness of ξ by comparison with ρ are satisfied within the limits of our required accuracy.

Neglecting ξ by comparison with ρ , we obtain the ignition condition in the simple form

$$\rho = \sqrt{\frac{\lambda E(T_1 - T_0)^2}{2F(T_1)RT_1^2}} \quad (11)$$

This relation connects the ignition gas temperature T_1 of the sphere with its radius ρ . The smaller the radius ρ the higher the temperature to which the sphere must be heated to bring about ignition of the gas.

Remembering that a^n is proportional to $(p/T)^n$, we obtain the relation between the critical pressure and the temperature at constant ρ

$$\lg \frac{p}{T_1} = \frac{0.217}{2T_1} E + C = \frac{A}{T_1} + C \quad (12)$$

that is, the expression is practically of the same type as for the self-ignition in a closed vessel (equations (9) and (10) of section I). There are, unfortunately, no systematic experimental data for checking these relations.

The relation between ρ and T may be given in the following form:

$$\lg \frac{\rho T_1}{T_1 - T_0} = \frac{0.217}{T_1} \left(\frac{E}{2} \right) + B \quad (13)$$

The relation between T_1 and ρ for the ignition of meth-

ane, illuminating gas and hydrogen in air were studied by Silver* with the aid of heated metal spheres of 1 to 5 millimeters diameter. Plotting $\lg p/(T_1 - T)$ against $1/T$, he obtained good straight lines. The value of E computed for methane was 40,000, and for hydrogen 45,000. The latter value was considerably below that which would have been obtained from kinetic data. The possibility is not excluded that Silver's results are impaired by the catalysis on the metal-sphere surface. The presence of catalytic action, according to both theoretical and experimental results, should have a strong effect on the ignition temperature. As a matter of fact, wires of different materials ignite the same gas at different temperatures. In particular, for a very strong catalytic action, ignition, as is known, does not, in general, occur and flameless combustion takes place. This is due to the fact that the reaction taking place at the heated catalyzing surface envelops the last layer of the reaction products, thus screening the heated layers from the burning gas and the molecules of the combustible burn by diffusion without any flame. It is very unfortunate that a problem as important as that of ignition has not yet been subjected to systematic experimental investigation. Such an investigation would permit not only confirmation of the theory but would provide very useful data on the character of the chemical reaction by determining E and n in the for-

mula $w = ka^n e^{-\frac{E}{RT}}$ within a very large temperature interval (since by varying the gas pressure and the wire diameter from 5 millimeters to 5μ we can vary the ignition temperature of the gas by a few hundred degrees).

It is not difficult to analyze the problem of ignition by heated wires (of radius ρ) coaxially placed inside a large cold cylinder (of radius $R \gg \rho$).

Reasoning in the same way as for the case of the sphere, we obtain the following relation between $\rho + \xi$ and T_1 :

$$(\xi + \rho) \ln \frac{R}{(\rho + \xi)} = \sqrt{\frac{E\lambda(T_1 - T_0)^2}{2F(T_1)RT_1^2}}$$

*Silver (cited by Jost, reference 2) gave an incorrect theory, from which his computed activation energies came out half as large.

$$\xi = \sqrt{\frac{2RT_1^2}{EF(T_1)}}; \quad \frac{\xi}{(\xi + \rho) \ln \frac{R}{(\rho + \xi)}} = \frac{2RT_1^2}{E(T_1 - T_0)} = \frac{1}{6}$$

which for $\frac{R}{(\rho + \xi)} \sim 10$ gives $\ln \frac{R}{(\rho + \xi)} \sim 2$, or

$$\frac{\xi}{(\xi + \rho)} \sim \frac{1}{3} \quad \text{whence, approximately}$$

$$\rho \ln \frac{R}{\rho} = \sqrt{\frac{E\lambda(T_1 - T_0)^2}{2F(T_1)RT_1^2}} \quad (14)$$

Thus far we have considered the cases of purely conductive heat transfer. We shall discuss the question of convection because there is a widely held view that hot-wire computations based on the equation of heat conduction from wires is not correct. By the convection assumption, the wire is surrounded by a cylindrical laminar gas layer within which the heat flows by conduction and at the boundary of this layer is at the temperature T_0 of the surrounding medium.

According to the experimental results the convective heat flow of cylinders (referred to unit area of the cylinder) is $q = \alpha (T_1 - T_0) = \frac{\lambda}{2\rho} A (T_1 - T_0)$, where A increases with increasing radius ρ of the wire. The value of the coefficient A according to the theory depends on the nondimensional parameter $B = \frac{d^3 \delta^2 g \Delta T}{\mu^2 T}$ where $d = 2\rho$, δ is the gas density, g the acceleration of gravity, μ the gas viscosity, ΔT the temperature drop $(T - T_0)$. (T is a certain mean value of the temperature between T_1 and T_0 .) It is found that on changing B from 10^{-5} to 10^3 , the value of A increases from 0.45 to 2.6; that is, five times.

We shall compute the value of B for a gas at atmospheric pressure, assuming $d < 1$ mm, $\delta = 10^{-3}$, $\mu = 10^{-4}$, $g = 10^3$, $\frac{\Delta T}{T} \sim 1$. We obtain $B < 10^2$; that is, for various diameters from 1 millimeter to $d = 1$, A changes from 1.7 to 0.5 (for $r = 0.1$, $A = 0.7$).

We can now compute the radius R' of the laminar layer within which the heat is transferred by conduction. Equating the total flow from a unit length of the wire $\pi\lambda A (T_1 - T_0)$ to the flow obtained from the solution of the problem of the heat conduction between two coaxial cylinders, we obtain

$$\pi\lambda A (T_1 - T_0) = \frac{2\pi\lambda (T_1 - T_0)}{\ln \frac{R'}{\rho}} \quad (15)$$

whence $\ln \frac{R'}{\rho} = \frac{2}{A}$, $A = 1.7$, $\ln \frac{R'}{\rho} = \frac{2}{1.7} \approx 1.2$ or

$R' = 3.2 \rho$, which gives for $\rho = 1$ mm, $R' = 3.2$; and

for $\rho = 0.1$ mm and $A = 0.7$, $\ln \frac{R'}{\rho} = \frac{2}{0.7} \approx 3$ and

$R' = 25 \rho = 2.5$ mm.

From formula (14) we see that for the radius R of the outside cylinder, the presence of convection shows up only in that in place of $\ln \frac{R}{\rho}$ we have $\ln \frac{R'}{\rho}$. For

$R = 3$ cm and $\rho = 1$ mm $\ln \frac{R}{\rho} \approx 3$ and $\ln \frac{R'}{\rho} \approx 1.2$. For

$\rho = 0.1$ mm $\ln \frac{R}{\rho} \approx 6$ and $\ln \frac{R'}{\rho} = 3$; that is, for the

accuracy which we require (of the order of 100 percent in determining the absolute values and of 10% in determining the ignition temperature), it is permissible to use the solution based on conduction for wires of radius of 1 millimeter and less.

We conclude by investigating the question of the composition of the combustible mixture near the wires at the ignition limit. Since the temperatures of very thin wires are high, the question arises as to whether the wire is practically surrounded by reaction products as in the case of a strongly catalyzing surface. Zeldovich, in his paper (unpublished) provides an answer to this question. It is found that the percent of reaction products in the gas near the igniting surface is always small since there is an intense diffusion of these products from the reaction zone toward the cool gas. We give the corresponding computation below.

The distribution b of the number of molecules of

the reaction products per unit volume and the temperature distribution between the plates are obtained from the equations

$$\lambda \frac{d^2 T}{dx^2} + w \frac{Q}{N} = 0$$

$$D \frac{d^2 b}{dx^2} + w = 0$$

Substituting for the variable T the variable $\theta = c' \frac{(T - T_0)N}{Q}$ and recalling that $D = \frac{\lambda}{c'}$, we rewrite the first equation in the form $D \frac{d^2 \theta}{dx^2} + w = 0$. It then follows that both variables, θ and b , satisfy the same equation. At some distance from the hot plate $T = T_0$ and $b = 0$; thus, for large x (for example, near the cold plate) $\theta = 0$ and $b = 0$. At the surface of the hot plate $\frac{db}{dx} = 0$ always because the noncatalyzing surface neither generates nor absorbs reaction products and hence the flow of material is equal to zero. When the temperature of the hot plate is near the ignition temperature (and only in this case) $(dT/dx)_0$ at the hot plate is equal to zero. Thus when we reach the ignition conditions the temperature field becomes similar to the field of concentration, since θ and b are defined by the identical equations and identical boundary conditions. Thus $\theta = b$ or $\frac{c'(T - T_0)N}{Q} = b$ at all points between the plates. If the number of initial molecules of the combustible mixture was a , then b will correspond to the temperature T determined by the equation

$$\frac{b}{a} = \frac{c'(T - T_0)N}{aQ}$$

The magnitude aQ/N is the total amount of heat generated per unit volume during explosion. The magnitude $c'(T - T_0)$ is the quantity of heat necessary to heat a unit volume of the gas to temperature T . We are interested in the extent of combustion at the wire itself, that is, in the magnitude

$$\frac{b_1}{a} = \frac{(T_1 - T_0) c' N}{a Q}$$

$\frac{c'}{a}$ is the heat capacity of a single molecule, $\frac{c'}{a} N$ the heat capacity of a gram molecule, whence $\frac{b_1}{a} = \frac{(T_1 - T_0) C}{Q}$, since $C \approx 5$, $\frac{b_1}{a} = \frac{(T_1 - T_0) 5}{Q}$. For $T_1 = 500^\circ$ and $Q = 3 \times 10^4$ $\frac{b_1}{a} \approx \frac{1}{30}$; that is, in all, 3 percent of the products of reaction are found in the mixture near the heated surface.

For $T_1 = 1300^\circ$ and $Q = 3 \times 10^4$ $\frac{b_1}{a} = \frac{5 \times 10^3}{3 \times 10^4} = 0.17$, that is, 17 percent. Thus, up to very high temperatures the percent of dilution by reaction products, even at the heated surface, is not large. The same relations as for wires hold for small heated spheres.

Translation by S. Reiss,
National Advisory Committee
for Aeronautics.

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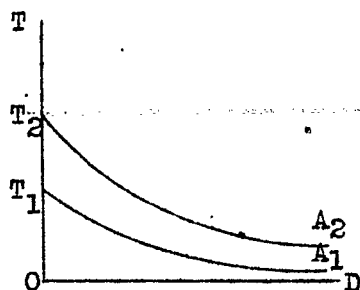


Figure 1.

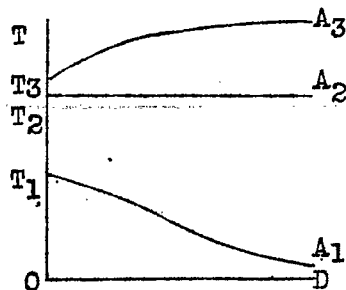


Figure 2

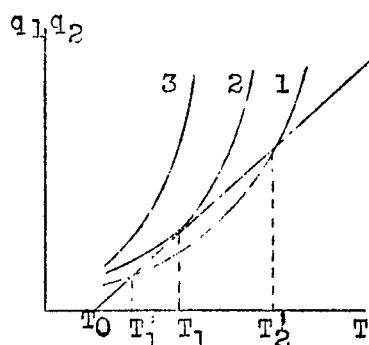


Figure 3

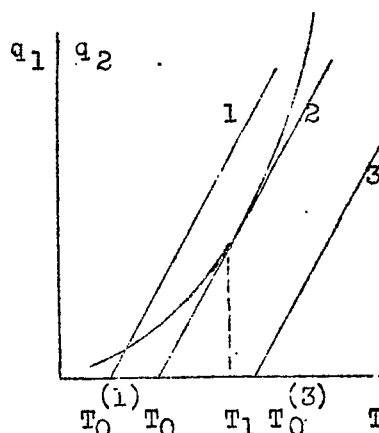


Figure 4

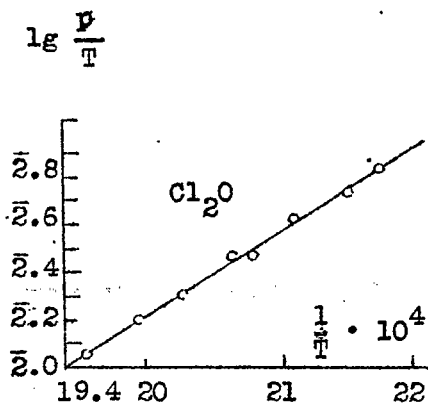


Figure 5

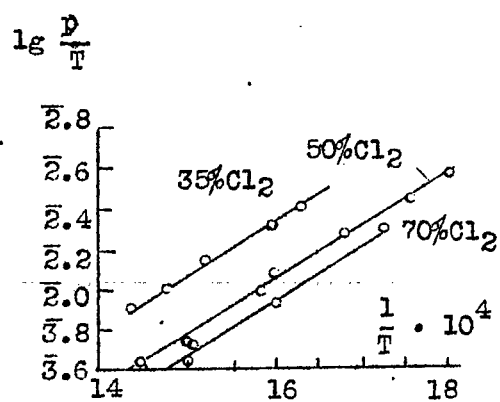


Figure 6

$$\lg \frac{k}{k_0} \quad \frac{p}{p_0}$$

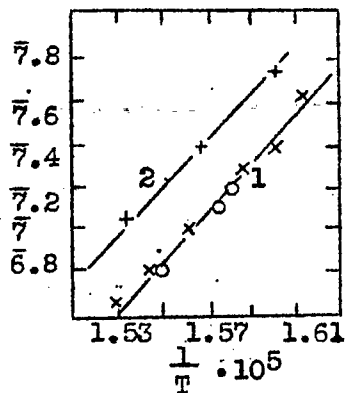


Figure 7

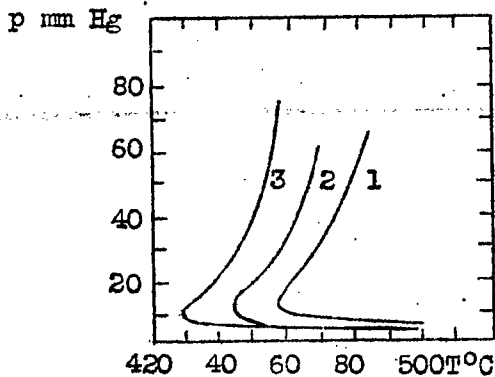


Figure 8

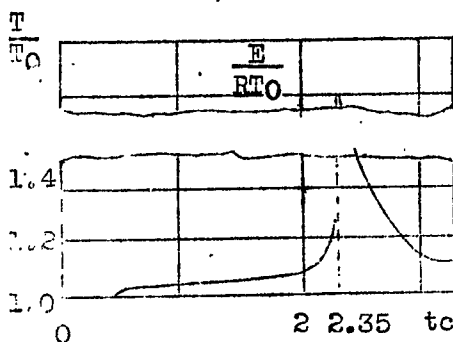


Figure 9

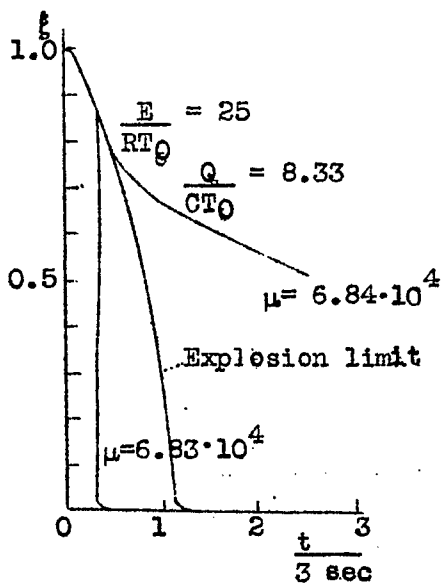


Figure 10

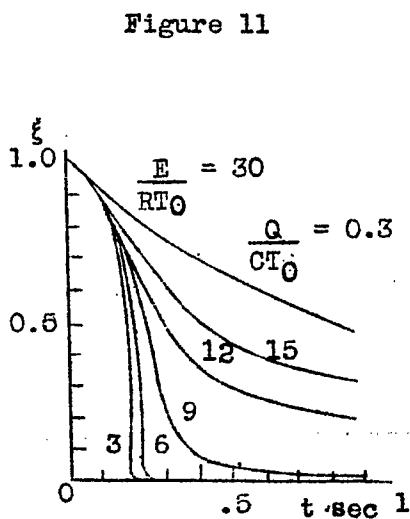


Figure 11

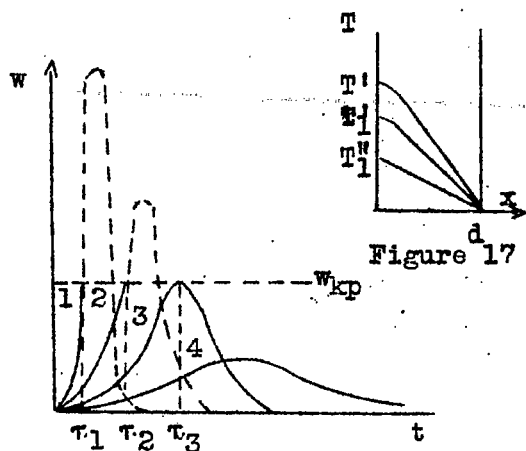


Figure 14

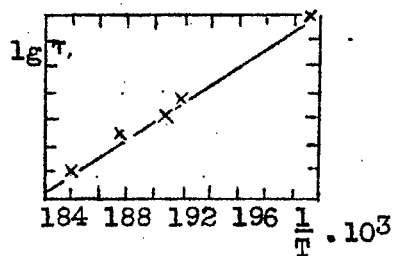


Figure 15

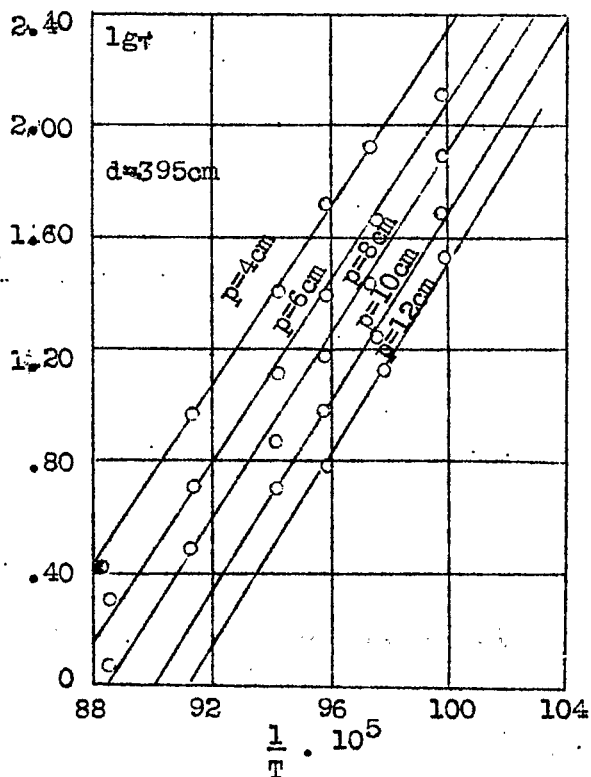


Figure 16

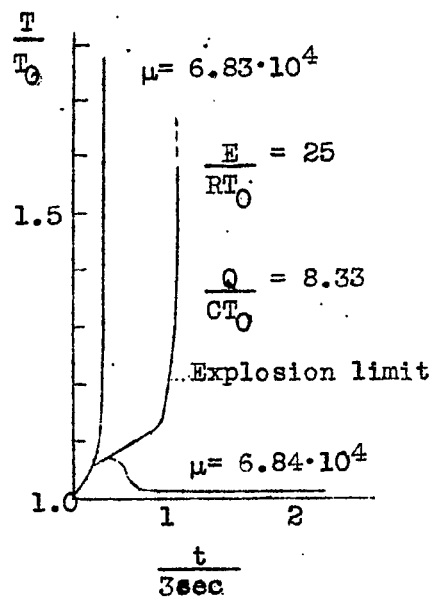


Figure 12

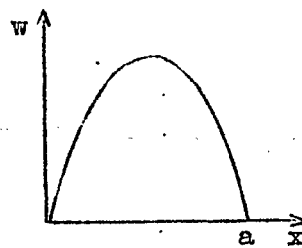


Figure 13

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